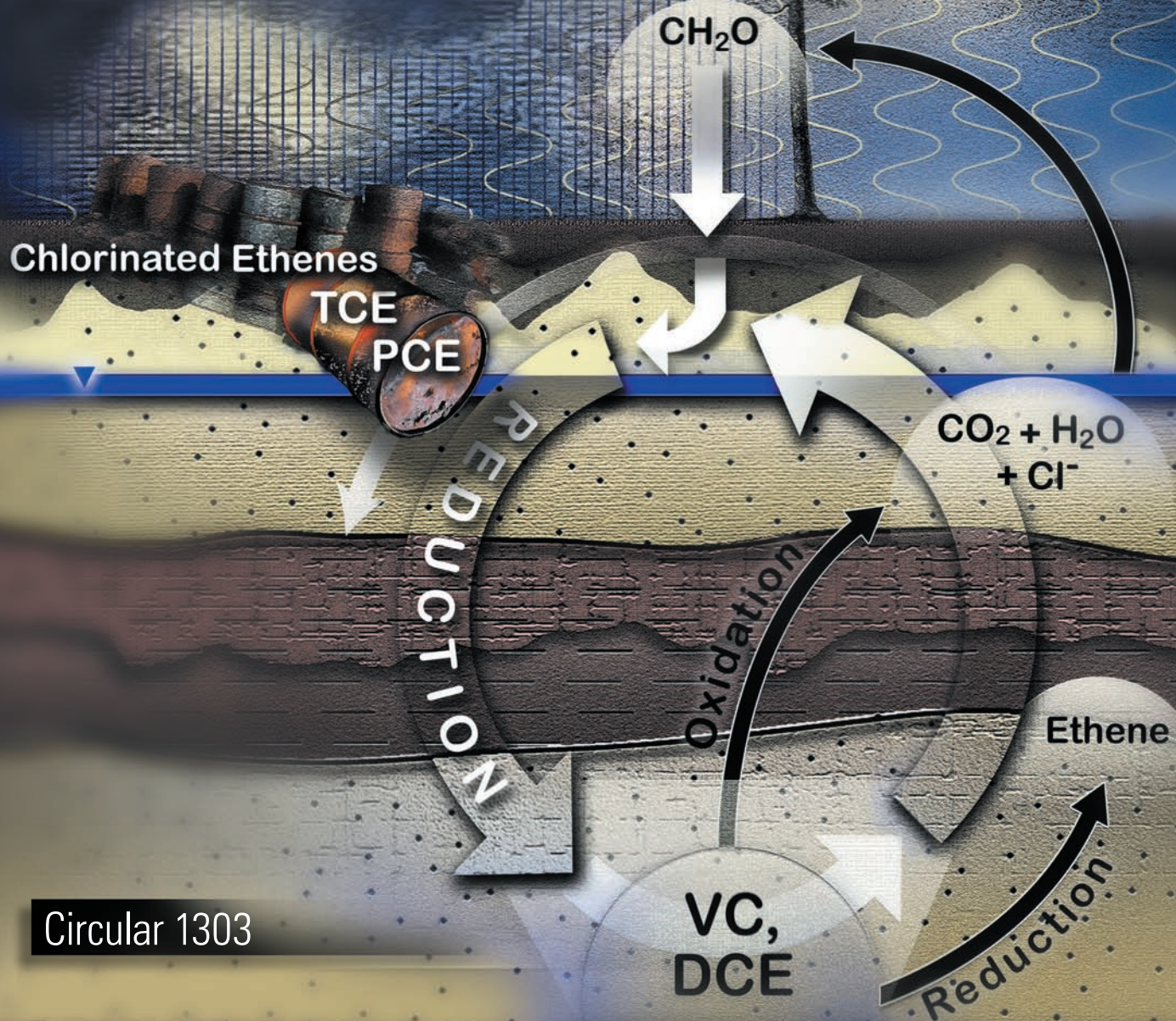


Toxic Substances Hydrology Program

Prepared in cooperation with the
Strategic Environmental Research and Development Program

A Framework for Assessing the Sustainability of Monitored Natural Attenuation



Circular 1303

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14. ABSTRACT

The sustainability of monitored natural attenuation (MNA) over time depends upon (1) the presence of chemical/ biochemical processes that transform wastes to innocuous byproducts, and (2) the availability of energy to drive these processes to completion. The presence or absence of contaminant- transforming chemical/biochemical processes can be determined by observing contaminant mass loss over time and space (mass balance). The energy available to drive these processes to completion can be assessed by measuring the pool of metabolizable organic carbon available in a system and by tracing the flow of this energy to available electron acceptors (energy balance). For the special case of chlorinated ethenes in ground-water systems, for which a variety of contaminant-transforming biochemical processes exist natural attenuation is sustainable when the pool of bioavailable organic carbon is large relative to the carbon flux needed to drive biodegradation to completion. These principles are illustrated by assessing the sustainability of MNA at a chlorinated ethene-contaminated site in Kings Bay, Georgia. Approximately 1,000 kilograms of perchloroethene (PCE) was released to a municipal landfill in the 1978?1980 timeframe, and the resulting plume of chlorinated ethenes migrated toward a nearby housing development. A numerical model, built using the sequential electron acceptor model code (SEAM3D), was used to quantify mass and energy balance in this system. The model considered the dissolution of non-aqueous phase liquid (NAPL) as the source of the PCE and was designed to trace energy flow from dissolved organic carbon to available electron acceptors in the sequence oxygen > chlorinated ethenes > ferric iron > sulfate > carbon dioxide. The model was constrained by (1) comparing simulated and measured rates of ground-water flow, (2) reproducing the observed distribution of electron-accepting processes in the aquifer, (3) comparing observed and measured concentrations of chlorinated ethenes, and (4) reproducing the observed production and subsequent dilution of dissolved chloride, a final degradation product of chloroethene biodegradation. Simulations using the constrained model indicated that an average flux of 5 milligrams per liter per day of organic carbon (CH₂O) per model cell (25 square meters) is required to support the short-term sustainability of MNA. Because this flux is small relative to the pool of renewable organic carbon (about 4.7 x 10⁷ milligrams [mg] per model cell) present in the soil zone and nonrenewable carbon (about 6.9 x 10⁸ mg per model cell) in an organic-matter-rich sediment layer overlying the aquifer, the long-term sustainability of MNA is similarly large. This study illustrates that the short- and long-term sustainability of MNA can be assessed by

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Appendix 1. Description of the Deterministic Model

The SEAM3D code uses mathematical models of contaminant loading and attenuation processes in order to provide a quantitative mass balance of the system. Advection refers to dissolved mass in groundwater, and is proportional to the velocity v [LT^{-1}] and the change of concentration with particular distance, x [L^{-1}]:

$$v \frac{\partial C}{\partial x}$$

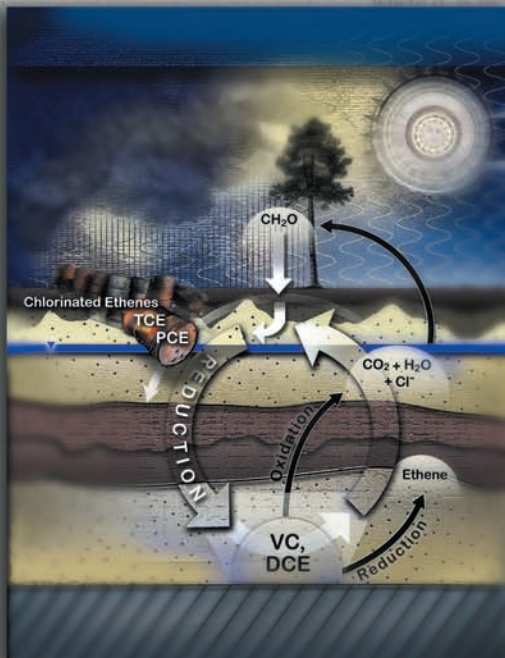
This advective term, therefore, has units of mass concentration per unit time [$ML^{-3}T^{-1}$]. The dispersion of dissolved mass in flowing ground water is proportional to the velocity and a velocity-dependent constant, the coefficient of dispersion, D [L^2T^{-1}], and the second derivative of concentration with distance:

$$D \frac{\partial^2 C}{\partial x^2}$$

Again, the units of this term are mass concentration per unit time [$ML^{-3}T^{-1}$]. Sorption refers to the distribution of mass between the aqueous and adsorbed phases and is described by the term:

$$\frac{\rho_b K_d}{n} \frac{\partial C}{\partial t}$$

where ρ_b is the bulk density of aquifer solids [ML^{-3}], K_d is the distribution coefficient (dimensionless), and K_d is a distribution coefficient between the adsorbed and aqueous phases. The units of this term are mass concentration per unit time [$ML^{-3}T^{-1}$].



Cover: Cyclic biodegradation of chlorinated ethenes (adapted from figure 4).

A stylized graphic on the left side of the cover features a sun with rays, partially obscured by a wavy line that suggests a horizon or a path. The background is a light beige color with subtle, larger-scale wavy patterns.

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Foreword

Natural attenuation, a series of naturally occurring processes that transform potentially dangerous environmental contaminants into innocuous byproducts, occurs to some degree in all hydrologic systems. The efficiency of natural attenuation, however, varies widely for different hydrologic environments and for different environmental contaminants. Monitored Natural Attenuation (MNA) is the regulatory term for the use of these naturally occurring processes to help manage human-generated wastes. Good environmental stewardship requires, however, that MNA be applied in a technically sound manner that reliably protects humans and wildlife from chemical contaminants.

Several years ago, the Strategic Environmental Research and Development Program (SERDP), a cooperative program of the Department of Defense, the Department of Energy, and the Environmental Protection Agency, initiated research designed to improve the scientific basis for evaluating MNA. Because MNA is often considered as a part of remediation systems that need to operate for decades or centuries, methods for understanding the long-term sustainability of MNA were of particular priority. SERDP, in partnership with the U.S. Geological Survey, Virginia Polytechnic Institute and State University, and Oak Ridge National Laboratory, initiated a project to assess the long-term sustainability of MNA. This report summarizes some of the findings of that study.

The results of this joint study highlight opportunities and potential dangers associated with applying MNA to contaminants such as chlorinated solvents. The principal opportunity is that microorganisms capable of cycling chlorinated solvents to innocuous byproducts (carbon dioxide and chloride) are ubiquitous and are present in all hydrologic systems. This, in turn, shows that MNA can be a useful tool for managing chlorinated solvents that have been released to the environment. The potential danger is that chemical energy, principally in the form of organic matter, is required to drive these degradation processes to completion—a requirement that is not met in some hydrologic systems.

This report outlines methodology for assessing the efficiency and sustainability of MNA. As such, it provides environmental managers a sound scientific basis for identifying sites where MNA is sustainable and an appropriate part of overall site remediation. Just as importantly, it also helps identify those sites where MNA may *not* be sustainable and not appropriate for site remediation. The principal mission of SERDP is to provide Federal facilities managers and regulators with sound, scientifically based information for implementing cost-effective environmental remediation. This report advances that mission.

Robert M. Hirsch
U.S. Geological Survey, Associate Director for Water

Bradley Smith
Strategic Environmental Research and Development Program, Executive Director

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Conversion Factors

Inch/Pound to Metric

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Volume		
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m ³)
Flow rate		
foot per second (ft/s)	0.3048	meter per second (m/s)
foot per day (ft/d)	0.3048	meter per day (m/d)
foot per year (ft/yr)	0.3048	meter per year (m/yr)
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)

Metric to Inch/Pound

Multiply	By	To obtain
Length		
meter (m)	3.281	foot (ft)
Area		
square meter (m ²)	0.0002471	acre
Volume		
cubic meter (m ³)	264.2	gallon (gal)
liter (L)	61.02	cubic inch (in ³)
cubic meter (m ³)	35.31	cubic foot (ft ³)
Flow rate		
meter per day (m/d)	3.281	foot per day (ft/d)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
Density		
gram per cubic centimeter (g/cm ³)	62.4220	pound per cubic foot (lb/ft ³)
Hydraulic conductivity		
meter per day (m/d)	3.281	foot per day (ft/d)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$

Abbreviations and Acronyms

AOC	Available organic carbon
A_r	Advection
ATP	Adenosine triphosphate
B_r	Biodegradation
CH_4	Methane
CH_2O	Organic carbon
$(CH_2O)_6$	Glucose
Cl	Chloride
C^v	NAPL mass in grams of NAPL per gram of sediment
CO_2	Carbon dioxide
DCE	Dichloroethene
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethene
DDT	Dichlorodiphenyltrichloroethane
DO	Dissolved oxygen
DOC	Dissolved organic carbon
D_r	Dispersion
EA	Electron acceptors
Fe(II)	Ferrous iron
Fe(III)	Ferric iron
H_2O	Water
LOI	Weight loss on ignition
LTSR	Long-term sustainability ratio
mg/L	Milligrams per liter
mM/L	Millimoles per liter
Mn(IV)	Solid-phase manganese
MNA	Monitored natural attenuation
$\mu\text{g/L}$	Micrograms per liter
NAC	Natural attenuation capacity
NAPL	Non-aqueous phase liquid
nM/L	Nanomoles per liter
NO_3	Nitrate
O_2	Molecular oxygen
PCE	Perchloroethene
P_r	Plant transpiration
SEAM3D	3-dimensional sequential electron acceptor model
SO_4	Sulfate
S_r	Sorption
STSR	Short-term sustainability ratio
TCE	Trichloroethene
TOR	Time of remediation
VC	Vinyl chloride
V_r	Volatilization

A Framework for Assessing the Sustainability of Monitored Natural Attenuation

By Francis H. Chapelle,¹ John Novak,² John Parker,³ Bruce G. Campbell,¹ and Mark A. Widdowson²

Abstract

The sustainability of monitored natural attenuation (MNA) over time depends upon (1) the presence of chemical/biochemical processes that transform wastes to innocuous byproducts, and (2) the availability of energy to drive these processes to completion. The presence or absence of contaminant-transforming chemical/biochemical processes can be determined by observing contaminant mass loss over time and space (mass balance). The energy available to drive these processes to completion can be assessed by measuring the pool of metabolizable organic carbon available in a system, and by tracing the flow of this energy to available electron acceptors (energy balance). For the special case of chlorinated ethenes in ground-water systems, for which a variety of contaminant-transforming biochemical processes exist, natural attenuation is sustainable when the pool of bioavailable organic carbon is large relative to the carbon flux needed to drive biodegradation to completion.

These principles are illustrated by assessing the sustainability of MNA at a chlorinated ethene-contaminated site in Kings Bay, Georgia. Approximately 1,000 kilograms of perchloroethene (PCE) was released to a municipal landfill in the 1978–1980 timeframe, and the resulting plume of chlorinated ethenes migrated toward a nearby housing development. A numerical model, built using the sequential electron acceptor model code (SEAM3D), was used to quantify mass and energy balance in this system. The model considered the dissolution of non-aqueous phase liquid (NAPL) as the source of the PCE, and was designed to trace energy flow from dissolved organic carbon to available electron acceptors in the sequence oxygen > chlorinated ethenes > ferric iron > sulfate > carbon dioxide. The model was constrained by (1) comparing simulated and measured rates of ground-water flow, (2) reproducing the observed distribution of electron-accepting processes in the aquifer, (3) comparing observed and measured concentrations of chlorinated ethenes, and (4) reproducing the observed production and subsequent dilution of dissolved chloride, a final degradation product of chloroethene biodegradation.

Simulations using the constrained model indicated that an average flux of 5 milligrams per liter per day of organic carbon (CH_2O) per model cell (25 square meters) is required to support the short-term sustainability of MNA. Because this flux is small relative to the pool of renewable organic carbon (about 4.7×10^7 milligrams [mg] per model cell) present in the soil zone and nonrenewable carbon (about 6.9×10^8 mg per model cell) in an organic-matter-rich sediment layer overlying the aquifer, the long-term sustainability of MNA is similarly large. This study illustrates that the short- and long-term sustainability of MNA can be assessed by:

1. Estimating the time required for contaminants to dissolve/disperse/degrade under ambient hydrologic conditions (time of remediation).
2. Quantifying the organic carbon flux to the system needed to consume competing electron acceptors (oxygen) and direct electron flow toward chloroethene degradation (short-term sustainability).
3. Comparing the required flux of organic carbon to the pool of renewable and nonrenewable organic carbon given the estimated time of remediation (long-term sustainability).

These are general principles that can be used to assess the sustainability of MNA in any hydrologic system.

Introduction

Monitored natural attenuation (MNA) is defined as the use of naturally occurring contaminant degradation, dispersion, and immobilization processes to reach site-specific remediation goals (Wiedemeier and others, 1996; U.S. Environmental Protection Agency, 1998, 1999). In current engineering practice, the effectiveness of MNA is evaluated on a site-by-site basis by considering three lines of evidence: (1) historical monitoring data showing decreasing concentrations and/or contaminant mass over time, (2) geochemical data showing that site conditions favor contaminant transformation or immobilization, or (3) site-specific laboratory studies documenting ongoing biodegradation processes (U.S. Environmental Protection Agency, 1998). Various field and laboratory methods for assessing these three lines of evidence have been developed and are currently in use (Wiedemeier and others, 1999).

¹ U.S. Geological Survey.

² Virginia Polytechnic Institute and State University.

³ U.S. Department of Energy.

For most sites, the effectiveness of chlorinated ethene natural attenuation is typically assessed over relatively short periods of time, often only a few months or years. When MNA becomes part of a long-term remediation strategy, however, it must be assumed that processes observed during site assessment will remain intact over the system's operational lifetime. This operational lifetime depends on the length of time that contaminants are released from source areas to ground water (National Research Council, 2000), a period of time that may encompass decades or even centuries. This, in turn, raises an important question. Will the natural attenuation processes observed during site assessment continue with the same efficiency in the future? In other words, will MNA be sustainable throughout the operational life of the remediation system?

A variety of circumstances affect the sustainability of MNA for chlorinated ethenes (Newell and Aziz, 2004), and thus, its sustainability can be expected to vary from site to site. In spite of this variability, the sustainability of MNA at any particular site should reflect the same set of general principles. The purpose of this report is to identify these general principles, arrange them into a framework suitable for assessing the sustainability of MNA, and illustrate these principles using a field example. This framework, in turn, leads directly to methods for characterizing and quantifying the sustainability of MNA that can be applied at any site.

Biological Cycles and the Nature of Sustainability

Life on Earth has been sustained for approximately 3.4 billion years. In considering the concept of sustainability, therefore, it is useful to begin with those characteristics of living systems that have made them sustainable for such long periods of time.

One characteristic of life systems is their cyclic nature. The use of carbon by living organisms, for example, is based on the alternate reduction of carbon dioxide (CO_2) and water (H_2O) to organic carbon (CH_2O) with the release of molecular oxygen (O_2) as a waste product. This oxygen, in turn, becomes a substrate for heterotrophic organisms that oxidize organic carbon back to carbon dioxide. Thus, the waste product (oxygen) of one biochemical process (photosynthesis) becomes the substrate (oxygen) for another biochemical process (heterotrophic metabolism). When the waste from one process becomes the substrate for another process, the result may be termed a *waste-substrate cycle*. Continuous, ongoing waste-substrate cycles, which are analogous to the action of a mechanical engine, are driven by the energy of the sun (fig. 1).

But while the overall stoichiometry of the carbon cycle is simple,

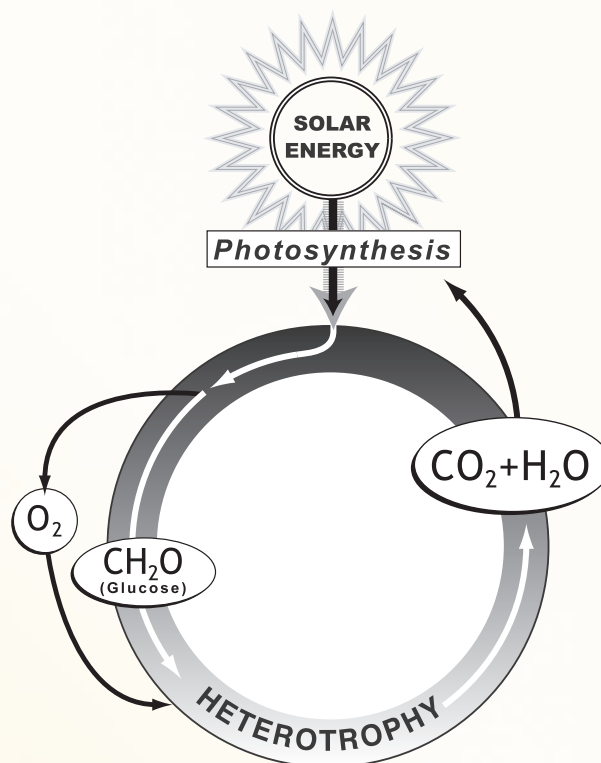
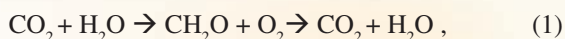


Figure 1. The carbon cycle.

the underlying biochemistry is enormously complex. Thousands of biochemical pathways are involved in the production of organic matter from carbon dioxide and solar energy. Similarly, there are just as many biochemical pathways that transform organic carbon back to carbon dioxide in order to complete the cycle.

Two well-known examples of heterotrophic biochemical pathways are glycolysis and the citric acid cycle (fig. 2). Glycolysis begins with the simple sugar glucose (CH_2O_6), which is sequentially fermented to pyruvate and carbon dioxide, yielding chemical energy in the form of adenosine triphosphate (ATP). At least nine enzymatically catalyzed steps are involved in glycolysis. Pyruvate formed by glycolysis can then enter the citric acid cycle, again undergoing numerous intermediate steps, with the final production of additional chemical energy (ATP) and CO_2 . The combination of glycolysis and the citric acid cycle results in the complete mineralization of glucose to carbon dioxide, and the conversion of chemical energy stored in glucose to ATP. Numerous biochemical pathways, of which glycolysis and the citric acid cycle are just two examples, have evolved over geologic time. In the absence of these enzymatically catalyzed biochemical processes, oxygen and organic carbon can coexist together indefinitely at room temperature and not be converted to carbon dioxide.

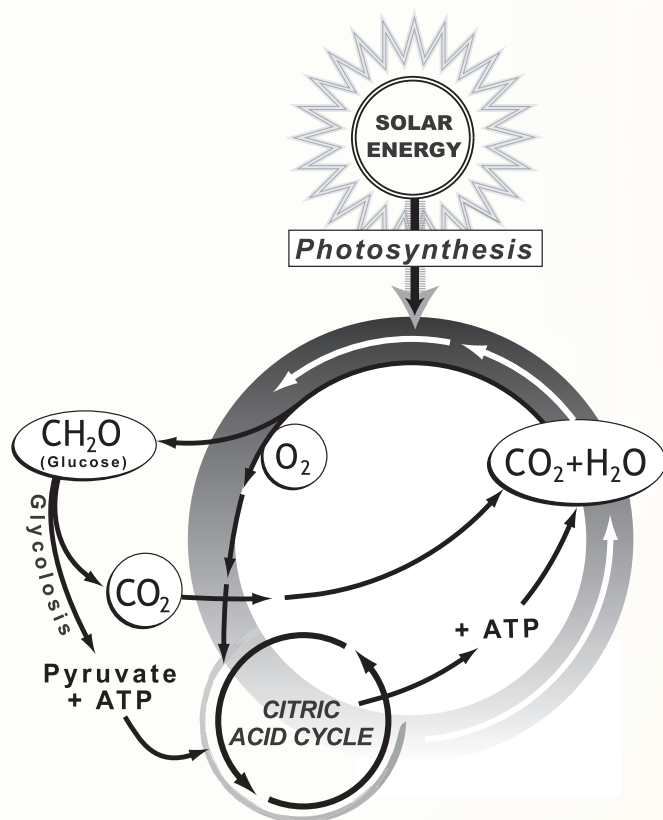


Figure 2. Role of biochemical pathways such as glycolysis and the citric acid cycle in the carbon cycle.

The carbon cycle in its present form, which has been sustained since the advent of biochemical photosynthesis 2.2 billion years ago, illustrates two important characteristics of sustainable biological systems. The first is that *biochemical mechanisms must be in place (glycolysis, the citric acid cycle) to transform the various carbon substrates that are available.* This is not a trivial requirement. All of these biochemical processes took long periods of time to evolve. The presence of biochemical mechanisms to perform certain functions, therefore, is not a given. Those that are present have evolved and developed over time, and they typically fill a particular available ecological niche.

The second characteristic of these biochemical pathways is that *energy must be available to drive the processes.* Biochemical pathways perform work in which organic molecules are assembled or disassembled, and work requires the utilization of energy. In the case of photosynthesis, it is the continuous delivery of solar energy that drives the carbon-oxygen cycle. Importantly, however, chemical energy stored in reduced carbon compounds also is available to drive biochemical pathways such as glycolysis and the citric acid cycle (fig. 2) that serve to complete the carbon cycle. These considerations suggest a working definition of sustainability:

A sustainable biological process is cyclic in nature, is based on existing biochemical mechanisms, and has a source of energy available to drive it over time.

This broad definition can be applied to the natural attenuation of human-generated contaminants. If particular contaminants (chlorinated ethenes) are actively transformed to innocuous products (carbon dioxide and chloride) by biochemical processes that are present in natural systems (reductive dechlorination, oxidation), and if energy (organic carbon) is available to drive these processes to completion, *then the natural attenuation of chlorinated ethenes is inherently sustainable.*

The converse of this definition also is true and is equally important. If biochemical processes are not present to transform contaminants, or if the available energy is not sufficient to complete this transformation, *then the natural attenuation of chlorinated ethenes is inherently unsustainable.* These definitions of sustainable and unsustainable natural attenuation are central to this report.

DDT—An Incomplete Waste-Substrate Cycle

In 1962, Rachel Carson published the book “Silent Spring” that described environmental damage caused by the unregulated use of pesticides such as DDT. This book, which marks the beginning of the modern environmental movement, showed how DDT was entering the food chain by agricultural spraying and was accumulating to harmful levels in some organisms. One example was the bioaccumulation of DDT in birds near the top of the food chain. In the case of bald eagles, DDT contributed to the production of fragile eggshells that tended to break during incubation of the eggs. This, in turn, nearly led to the extinction of bald eagles in the continental United States. If the use of DDT continued, Carson argued, then more bird species would be adversely affected and humans would be faced with the prospect of springtime in which there were no singing birds—a silent spring. Because “Silent Spring” has been so influential in the modern environmental movement, because DDT is a chlorinated compound, and because DDT was the first human-produced chemical to be banned for environmental reasons in the United States, it is useful to consider DDT in the context of natural attenuation and sustainability.

Dichlorodiphenyltrichloroethane (DDT) was originally developed during World War II as a treatment for body lice on humans. The bacterium *Rickettsia prowazekii* is part of the normal flora of the common body louse, and causes the disease typhus in humans. During World War II, unsanitary conditions led to the proliferation of lice in human populations, and millions of people were threatened by typhus. DDT in powdered form is highly toxic to body lice and other insects. Because it is virtually insoluble in water, however, DDT can be applied externally to the skin in controlled amounts that are not toxic to humans. The introduction of DDT as a de-lousing agent in 1943 and later its use to control malaria-spreading mosquitoes is estimated to have saved as many as 500 million human lives (National Academy of Science, 1970).

The later use of DDT as an agricultural pesticide, however, a practice that began in the late 1940s, initiated the adverse environmental effects described by Rachel Carson and others. Specifically, DDT was not observed to degrade once it was released into the environment, and it accumulated in soils and aquatic sediments. In addition, fat-soluble DDT also tended to bioaccumulate as it was passed up the food chain, eventually reaching levels that could be harmful to birds and mammals. These adverse effects led to bans on DDT use, first in Sweden (1970) and then in the United States (1972).

One way to consider the observed behavior of DDT in the environment is in the context of sustainable natural attenuation. Even though DDT has not been used in the United States in 35 years, it remains a common contaminant of aquatic sediments (Van Metre and Mahler, 2004). The reason DDT persists in the environment has to do with its chemical structure. The combination of two linked chlorinated phenols with a chlorinated ethane is a chemical structure not commonly found in nature. Consequently, biochemical mechanisms capable of cycling DDT to carbon dioxide and chloride have not evolved in natural ecosystems. Soil and sediment microorganisms are able to partially dechlorinate DDT to dichlorodiphenyldichloroethene (DDE) and then to dichlorodiphenyldichloroethane (DDD). But this process attacks only the chlorinated ethane portion of the DDT molecule and happens only under highly reducing conditions. Under the aerobic conditions characteristic of many agricultural soils, biochemical mechanisms are not present to transform DDT to innocuous products such as carbon dioxide and chloride (fig. 3). Consequently, DDT, DDE, and DDD commonly accumulate in the environment, in some cases reaching toxic levels. Because of the lack of DDT-transforming biochemical pathways, *the natural attenuation of DDT in aerobic soils is by definition unsustainable*.

The lack of sustainable DDT natural attenuation is due to the lack of specific chemical/biochemical mechanisms available for transforming the waste. Equally important, however, is the case where transforming biochemical mechanisms are present, but where sufficient energy to complete the cycle is not available. An example of this behavior is given by highly chlorinated ethenes such as perchloroethene (PCE) and trichloroethene (TCE).

Chlorinated Ethenes in an Oxygenated Aquifer—An Incomplete Waste-Substrate Cycle

In the late 1970s, an unusually large number of children living in Woburn, Massachusetts, developed childhood leukemia, and several of these children eventually died. Painstaking investigation finally showed that the incidence of leukemia was associated with drinking water produced from two municipal wells drilled into the underlying buried-valley aquifer (Harr, 1995). Analysis of the well water showed that it was contaminated by PCE and TCE. While both of these chemicals had been used for years as solvents and for dry cleaning,

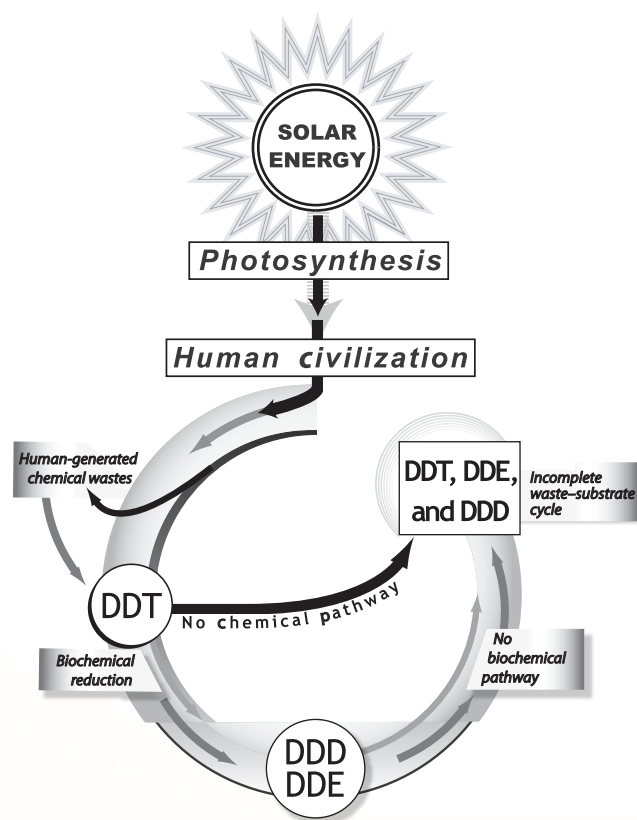


Figure 3. DDT as an example of an incomplete waste-substrate cycle.

few Americans had ever heard of them. Furthermore, the fact that these contaminants had migrated to Woburn's municipal wells led many people to the logical assumption that PCE and TCE, like DDT, did not biodegrade in the environment. After all, PCE and TCE, like DDT, did not occur naturally in the environment and were manufactured exclusively by human chemical technology. Why would naturally occurring microorganisms have the enzymatic capability to degrade chemicals like PCE and TCE?

But as the extent of ground-water contamination by chlorinated ethenes gradually was recognized in the early 1980s, it became apparent that other chlorinated ethenes such as dichloroethene (DCE) and vinyl chloride (VC) were often present in contaminated water. In many cases, these compounds were not present in the original contaminants, suggesting that DCE and VC were degradation products of PCE and TCE. Subsequent research established that PCE and TCE were subject to a variety of biodegradation processes including aerobic cometabolism (Wilson and Wilson, 1985) and anaerobic reductive dechlorination (Vogel and others, 1987). Later, it was also discovered that DCE and VC, the byproducts of reductive dechlorination, also were subject to both aerobic (Hartmans, 1995) and anoxic mineralization (Bradley and Chapelle, 1996).

Numerous naturally occurring biochemical pathways are now recognized to exist, and these pathways are capable of completely transforming chlorinated ethenes to innocuous byproducts such as carbon dioxide and chloride (fig. 4). Furthermore, these biochemical pathways appear to have evolved so that microorganisms can utilize natural chlorinated organic compounds that are ubiquitous in aquatic environments (Grimvall, 1995; Bradley, 2000, 2003). While these naturally occurring biochemical pathways are not fully transferable to all human-produced chlorinated compounds (such as DDT), they are transferable to chlorinated ethenes. Thus, the first requirement for a completed waste-substrate cycle—biochemical processes capable of transforming chlorinated ethenes to innocuous byproducts—has been met.

Establishing a waste-substrate cycle that is inherently sustainable, however, also requires the availability of energy. In the case of chlorinated ethenes such as PCE and TCE, this energy must be present in the form of organic carbon. Organic carbon acts as an electron donor in the metabolism of PCE and TCE, degrading microorganisms such as *Dehalococcoides* (DiStefano and others, 1991), in which PCE and TCE act as electron acceptors (fig. 4). The establishment of completed, sustainable waste-substrate pathways, therefore, requires the presence of sufficient chemical energy in the form of organic matter to drive the reductive dechlorination of PCE and TCE. When sufficient organic matter is available, chlorinated ethenes are subject to a completed waste-substrate cycle. Conversely, when sufficient organic matter is not available, the waste-substrate cycle cannot be completed, and chlorinated ethenes will persist.

This explains the persistence of PCE and TCE in the aquifer underlying Woburn, Massachusetts, and the subsequent transport of these chemicals to the municipal wells. The underlying buried-valley aquifer consists of sands and gravels that were deposited by retreating glaciers at the end of the ice ages about 15,000 years ago. Partly because of the cold climatic conditions that prevailed at that time, and partly because the sediments have been extensively reworked by flowing water, these sands and gravels contain little natural organic carbon. The amount of available organic carbon present in this glacial aquifer, and thus the energy that is available, is not sufficient to drive reductive dechlorination. The most obvious indication of this is that ground water in the glacial outwash aquifer contains relatively high concentrations of dissolved oxygen. Thus, the flux of dissolved oxygen into the aquifer with recharging ground water exceeds oxygen consumption by carbon-utilizing heterotrophic bacteria. This, in turn, diverts available chemical energy away from chlororespiration resulting in the observed accumulation of PCE and TCE. Even though contaminant-transforming biochemical mechanisms may be present, the waste-substrate cycle for PCE and TCE is not completed in oxygenated systems because of the lack of available energy.

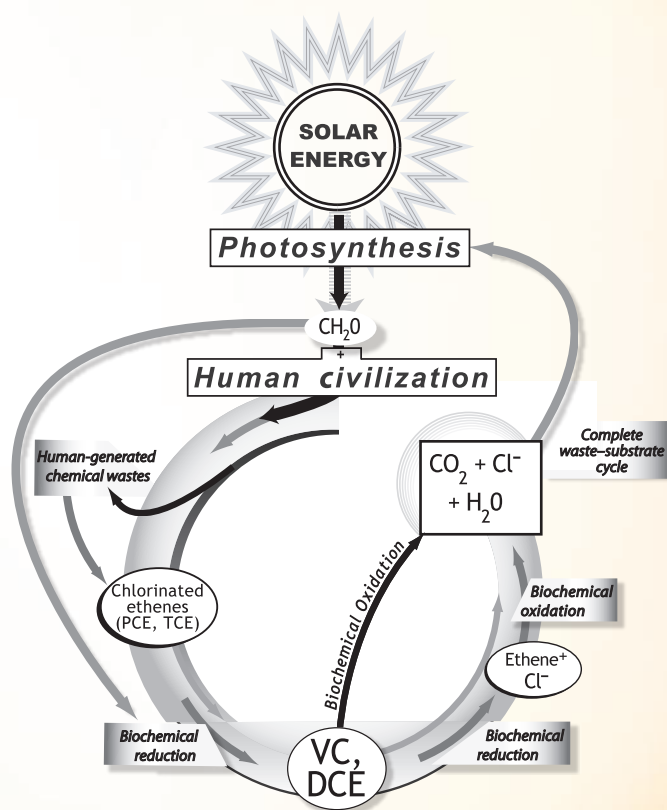


Figure 4. Biochemical cycling of chlorinated ethenes.

Chlorinated Ethenes in an Anoxic Aquifer—A Completed Waste-Substrate Cycle

Cases of environmental contamination such as Woburn, Massachusetts, where an incomplete waste-substrate cycle results in the exposure of humans to contaminants, are those that most often lead to adverse health affects in humans. Many other hydrologic systems, however, do contain sufficient organic matter to complete the waste-substrate cycle for PCE and TCE.

An example of this behavior was described at the Kings Bay Naval Submarine Base in southeastern Georgia (Chapelle and Bradley, 1998). This particular aquifer was deposited in a temperate marine environment that supported abundant photosynthesis, resulting in the deposition of large amounts of organic carbon. As is common in marginal marine sediments, however, the distribution of this sedimentary organic carbon varies depending upon the sedimentary depositional environment. Beach sands, for example, typically are organic-matter poor since the action of wind and surf tends to remove sedimentary organic matter from them. Back-bay deposits, on the other hand, which are deposited in relatively quiet

lagoons between barrier islands (beaches) and the mainland, commonly contain large amounts of organic matter. As these sedimentary units are deposited by prograding shorelines, organic-matter-poor barrier island sands are typically overlain by organic-matter-rich back-bay sediments. A photograph of an outcrop of the organic-matter-rich semiconfining bed, taken 2 miles from the Kings Bay site, is shown in figure 5. As rain-water percolates through the organic-matter-rich sediments and recharges the underlying beach-sand aquifer, dissolved oxygen is consumed. In addition, sedimentary organic matter can be partially dissolved and transported to the aquifer. The presence of dissolved organic matter and the absence of oxygen result in conditions favorable to reductive dechlorination and leads to efficient biodegradation of PCE at the Kings Bay site.

The Kings Bay site is an example of a system where the availability of energy in the form of sedimentary organic carbon is sufficient to drive the chlorinated ethene waste-substrate cycle to completion (fig. 4). This completed waste-substrate cycle stands in marked contrast to organic-matter-poor systems such as Woburn, Massachusetts, where the amount of available organic matter is insufficient to drive the waste-substrate cycle to completion.

Mass Balance, Energy Balance, and the Sustainability of Natural Attenuation

The different biodegradation patterns exhibited by chlorinated ethenes at the Woburn, Massachusetts, and the Kings Bay, Georgia, sites illustrate how the sustainability of natural attenuation processes can differ in ground-water systems. In both systems, microorganisms with the capability of degrading chlorinated ethenes were present, although probably in differing abundances. At one site (Woburn) the lack of energy to drive reductive dechlorination caused the preservation and accumulation of TCE and PCE in ground water. In the other system (Kings Bay), sufficient energy was available to drive reductive dechlorination, and thus, natural attenuation has been sustained for at least 30 years. This, in turn, helped to restrict the migration of environmental contaminants and contributed to overall site remediation (Chapelle, Bradley, and Casey, 2005). Clearly, it is useful to distinguish hydrologic systems characterized by sustainable or unsustainable natural attenuation for chlorinated ethenes. Methods for making such distinctions can be derived from the twin principles of mass and energy balance.



Figure 5. Photograph of the organic-matter-rich semiconfining bed overlying the semiconfined aquifer.

Mass and Energy Balance

Some of the ways in which mass and energy balance affect the sustainability of MNA are illustrated in figure 6. The reality is that human activities lead to the production of wastes, and these wastes may be released to the environment. Once released, wastes typically partition between soils, surface-water, and ground-water systems where they are subject to chemical and/or biochemical processes that (in some cases) transform these wastes to innocuous byproducts. If the rate of transformation equals or exceeds the rates of waste loading, then the natural attenuation processes have met the short-term criterion of sustainability (presence of chemical/biochemical processes capable of detoxifying chemical wastes). Conversely, if the rate of contaminant loading exceeds transformation rates, then the natural attenuation processes are by definition unsustainable. These different outcomes can be recognized by *the degree of accumulation*

or *non-accumulation of wastes* in the environment. Thus, the short-term requirement for sustainable natural attenuation can be recognized by *mass balance* considerations.

The sustainability of natural attenuation processes, however, does not end here. In addition to having chemical/biochemical processes that transform wastes to innocuous byproducts, sufficient energy must be available in the system to drive these processes to completion. For the case of chlorinated ethenes, this energy must be provided by an external source of carbon. Furthermore, the energy provided by the organic carbon must not be diverted by competing biochemical processes (such as oxygen-based respiration) away from contaminant-degrading processes. For petroleum hydrocarbons, the waste itself provides the source of energy driving degradation. In this case, a supply of electron acceptors must be available to facilitate energy flow. In both cases, however, the long-term requirement for sustainable natural attenuation can be recognized by *energy balance* considerations (fig. 6).

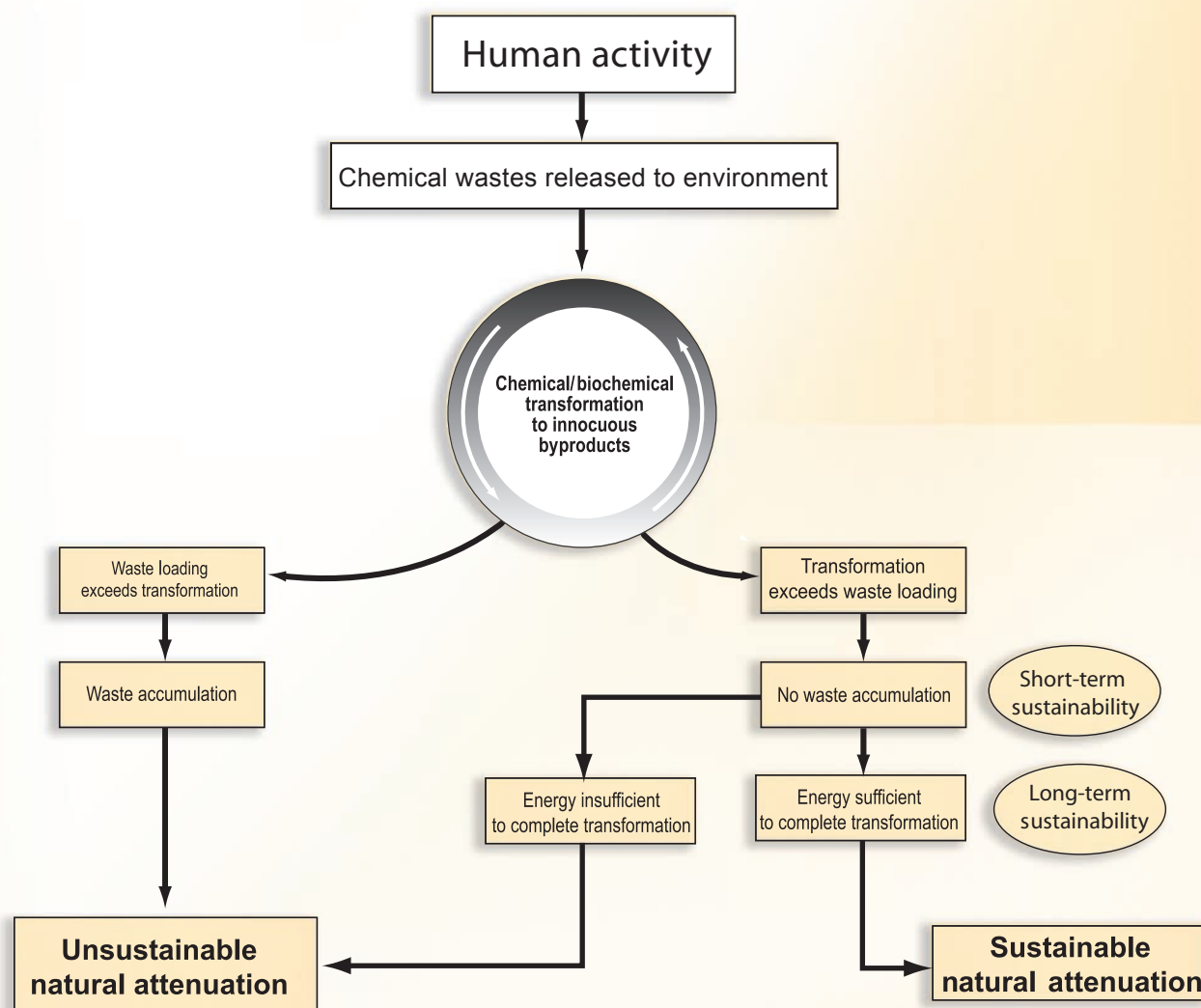


Figure 6. Effect of mass and energy balance on the sustainability of natural attenuation.

Defining the sustainability of MNA in terms of mass balance (short-term) and energy balance (long-term) immediately suggests ways for assessing the sustainability of MNA in different hydrologic systems. First, documenting the accumulation or non-accumulation of particular wastes (is the contaminant plume stable, shrinking, or enlarging) in a hydrologic system addresses short-term sustainability. Secondly, it suggests that evaluating energy sources available to drive waste transformation processes for the length of time required to fully transform contaminants addresses long-term sustainability.

Mass Balance in Contaminated Ground-Water Systems

The *efficiency* of natural attenuation can be defined in terms of a balance between the delivery to, and removal of, contaminants from ground-water systems by naturally occurring processes. This is most readily illustrated by considering the classic interaction between a contaminant source area, a dissolved plume emanating from the source area, and the attenuation of that plume (fig. 7). In most systems, contaminant mass in source areas is present in a variety of forms that include non-aqueous phase liquids (NAPL), chemically sorbed mass, or contaminant mass that has diffused into low-permeability clays, shales, or other rocks. Regardless of how it is stored, however, the contaminant mass tends to dissolve from these sources, enters aqueous solution, and forms plumes. The sum of the processes contributing dissolved contaminant mass to water (NAPL dissolution, desorption, diffusion) represents the *contaminant loading* component of the mass balance. Once formed, contaminant masses in plumes are subject to transport and natural attenuation processes that include advection (A_r), dispersion (D_r), biodegradation (B_r), sorption (S_r), volatilization (V_r), and plant transpiration (P_r) processes. The sum of these dispersive and removal processes represents the *natural attenuation capacity* component of the mass balance.

This conceptualization illustrates how the balance between contaminant loading and natural attenuation capacity determines the size of plumes, and thus their environmental impact. It may seem intuitively obvious that low contaminant loading

will lead to the development of a small plume; however, high contaminant loading combined with a high natural attenuation capacity also can result in a relatively small plume. Thus, the overall size of a plume does not necessarily distinguish between cases of small contaminant loading and cases of large natural attenuation capacity. When a site is sufficiently well-instrumented so that the contaminant loading and natural attenuation capacity can be assessed by direct observation, these differences become evident.

Energy Balance in Contaminated Ground-Water Systems

The efficiency of natural attenuation processes also depends upon the energy balance of ground-water systems. Reductive dechlorination requires the transfer of electrons from electron donors such as organic carbon, to chlorinated ethenes or other chlorinated organic compounds. If sources of electrons are lacking in a system, or if available electrons

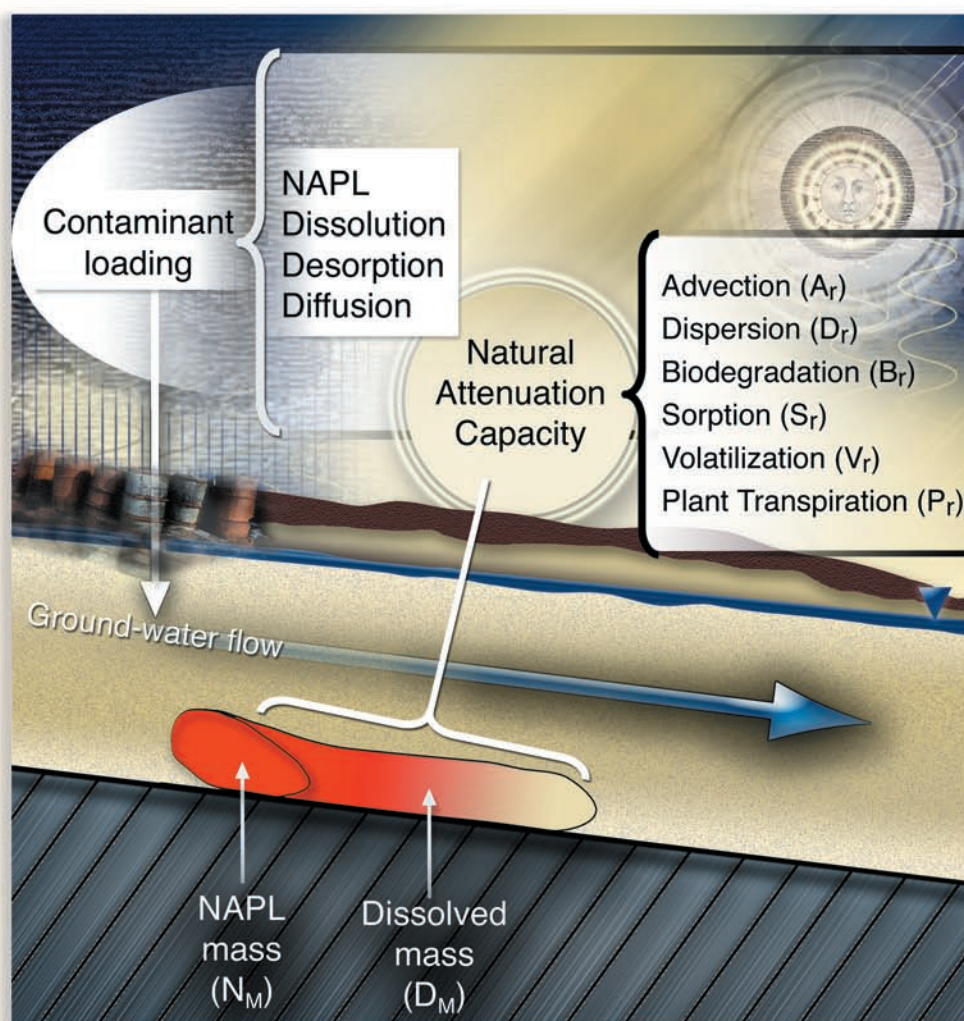


Figure 7. Interaction between a contaminant source area, a dissolved plume, and natural attenuation.

are diverted away from chlorinated ethene reduction, natural attenuation will not be sustainable.

Examples of ways that energy flow in ground-water systems affects the transformation of chlorinated ethenes are illustrated in figure 8. As organic matter oxidizes, electrons are transferred to available electron acceptors such as oxygen, nitrate, chlorinated ethenes, manganese [Mn(IV)], ferric iron [Fe(III)], sulfate, or carbon dioxide. Because the electronegativity of these compounds differs, their efficiency as electron acceptors differs as well. Dissolved oxygen typically is the most efficient electron acceptor present in the environment, so microorganisms gain more energy coupling organic-matter oxidation to oxygen reduction than other electron acceptors. If oxygen is available, ambient microorganisms will preferentially use oxygen.

Once oxygen is consumed, a condition that is common in subsurface environments isolated from the atmosphere, nitrate is the next most efficient electron acceptor commonly available. Nitrate is followed, in succession, by solid manganese oxides, solid ferric oxyhydroxides, dissolved sulfate, and finally carbon dioxide (fig. 8). Highly chlorinated ethenes such as PCE and TCE, which contain highly electronegative chlorine, also are potential electron acceptors in contaminated ground-water systems. This chlororespiration produces DCE, VC, and ethene as daughter products.

The ecological succession of electron-accepting processes (fig. 8) channels the flow of electrons, and thus the flow of energy, in predictable ways. For example, if excess dissolved oxygen is available in an aquifer, oxygen will sequester much of the electron flow from organic-matter degradation, effectively short-circuiting reductive dechlorination and leaving

PCE and TCE largely untransformed. Conversely, if Fe(III), sulfate, or carbon dioxide are the predominant electron acceptors present, PCE and TCE can intercept a portion of the overall electron flow. This, in turn, transforms PCE and TCE to DCE, VC, or ethene. The potential for transformation of PCE and TCE, therefore, depends both on a source of electron donors capable of supporting microbial metabolism, and conditions that allow chlorinated ethenes to intercept part of the overall electron flow. In other words, the sustainable transformation of chlorinated ethenes depends upon the energy balance of the system.

Quantifying Mass and Energy Balance

There are two philosophically distinct, but equally useful, approaches to quantifying mass and energy balance in ground-water systems. The first approach is *empirical* in nature and uses monitoring data to directly calculate the mass loading of contaminants to a system and the system's natural attenuation capacity. Similarly, the energy flow through a ground-water system can be empirically determined by evaluating the succession of electron-accepting processes. The second approach is *deterministic* in nature, quantifying mass and energy balance in terms of equations that describe the physics and biochemistry of a system. Both approaches have advantages and disadvantages. In practice, it is often useful to combine these approaches in order to address site-specific questions. These approaches can be illustrated using the Kings Bay site in Georgia as an example.

An Empirical Approach to Mass and Energy Balance

The empirical approach to contaminant mass balance (Chapelle, Campbell, and others, 2005) is illustrated in figure 9. Given a well-characterized plume, the flux of contaminants across a given cross-sectional transect of an aquifer can be estimated from the equation:

$$\text{mass flux}_{\text{transect}} = (C_{\text{ave}}) \times (Q), \quad (2)$$

where C_{ave} is the average contaminant concentration (in micrograms per liter), and Q is the ground-water flux in units of length per unit time (LT^{-1}). When this flux is summed over a given transect of the aquifer, it gives $\text{mass flux}_{\text{transect}}$ in units of mass per unit time (MT^{-1}). The ambient natural attenuation capacity (NAC) of the system can then be quantified as the difference in contaminant mass flux between two transects:

$$\text{NAC} = (\text{Mass flux}_{\text{transect 1}}) - (\text{Mass flux}_{\text{transect 2}}). \quad (3)$$

In this formulation, NAC is expressed in units of contaminant mass attenuated per unit time (MT^{-1}).

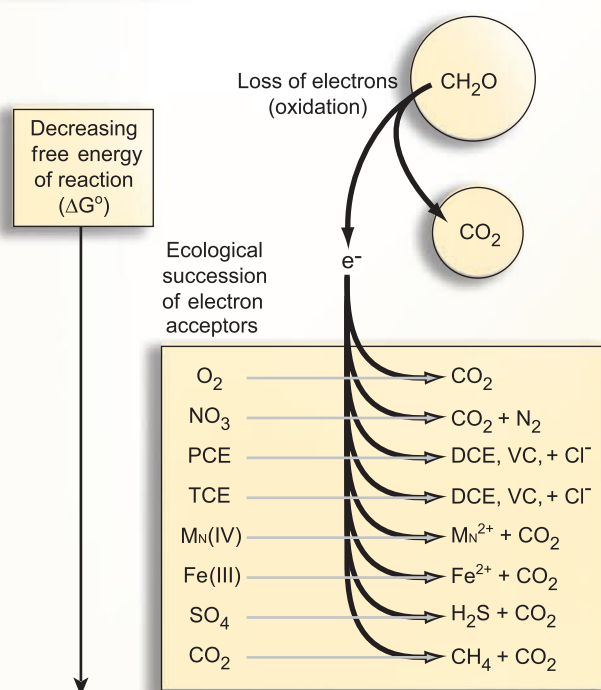


Figure 8. Ways in which energy flow in ground-water systems affects the transformation of chlorinated ethenes.

In principle, this empirical approach also can be used to assess the energy balance of a system. The large number of potential electron donors and electron acceptors present in ground-water systems makes this a difficult problem. The observed succession of electron-accepting processes (fig. 8), however, provides a framework for distributing energy flow in a predictable way. Empirically, energy flow can be assessed by observing the consumption of different electron acceptors as ground water flows downgradient (fig. 9). The overall flux of energy to particular electron-accepting processes then can be assessed using equations 1 and 2.

The chief advantage of using the empirical mass-balance approach is that no a priori assumptions need be made about the processes contributing to contaminant loading, contaminant attenuation, or the consumption of electron donors and acceptors. As a description of the present behavior of a system, therefore, the empirical approach is highly useful. Because the individual processes contributing to contaminant loading and natural attenuation are not explicitly considered, however, the

empirical approach cannot predict how a system will respond if conditions change at some point in the future. Thus, the utility of the empirical approach for assessing long-term questions, such as the sustainability of natural attenuation, is limited.

A Deterministic Approach to Mass and Energy Balance

Mass and energy balance in ground-water systems also can be quantified by considering the individual processes that deliver, transport, transform, partition, or sequester mass and energy in ground-water systems. Numerous processes including advection, hydrodynamic dispersion, sorption, and biodegradation affect the mass and energy balance of solutes being transported by ground-water flow (fig. 6). The deterministic approach uses mathematical equations to represent each individual process, and then sums the processes to obtain a set of coupled mass and energy balance equations. These equations

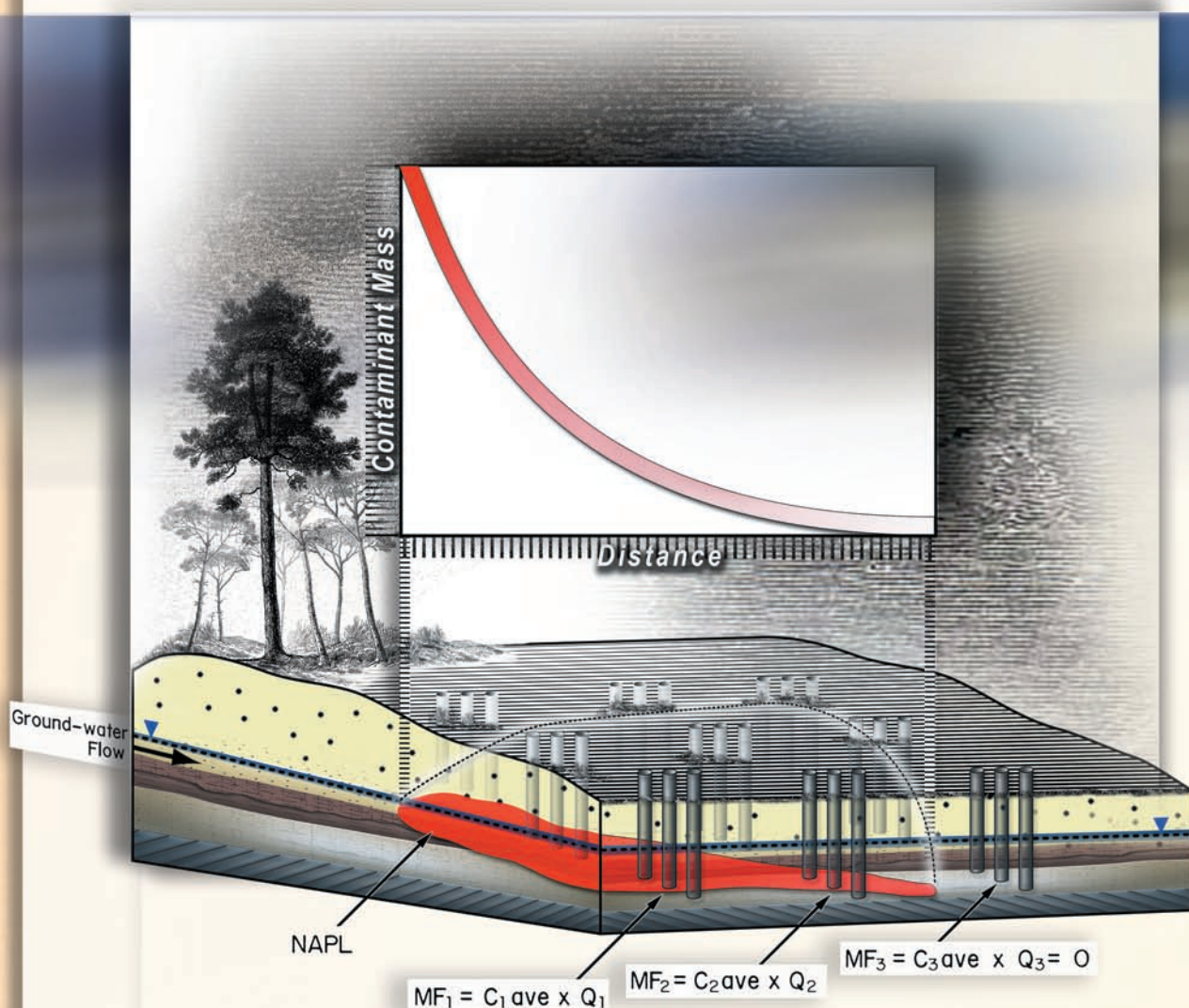


Figure 9. The empirical approach to describing the mass balance of a system depends on site-specific monitoring data.

then can be solved simultaneously to evaluate the interactions of contaminants, electron donors, and electron acceptors over time for a variety of specified environmental conditions. The chief advantage of this deterministic approach is that it provides time-dependent mass and energy balances which then can be used to assess how a system may respond if conditions change over time. This approach is well-suited, therefore, for assessing the long-term sustainability of natural attenuation.

In this report, the 3-dimensional Sequential Electron Acceptor Model (SEAM3D) was used to quantify mass and energy balance (Waddill and Widdowson, 1997). This model was selected because it explicitly calculates a mass balance for the amount of contaminant NAPL present in a system, and because it tracks the flow of energy from electron donors (organic carbon) and the various competing electron accepting processes. This, in turn, makes it possible to simultaneously track the dissolution of NAPL over time, and to couple the biotransformation of dissolved contaminant mass to the organic carbon and electron acceptors available in an aquifer. A detailed description of the SEAM3D code is provided in Appendix 1.

The description of SEAM3D given in Appendix 1 shows that, in order to use a deterministic approach for quantifying mass and energy balance at any given site, a large number of parameters describing NAPL dissolution, advective and dispersive transport of contaminants, biotransformation of contaminants, and the delivery and utilization of electron donors and acceptors are required. The model-building process begins with conceptualizing the hydrologic system, moves to estimating values for the various parameters required, and then constrains these estimated values by using available hydrologic, geochemical, and microbiologic data. Once the model has been adequately constrained, it can be used to evaluate how the sustainability of natural attenuation in a particular hydrologic system responds to various environmental conditions over time.

Conceptual Model of the Kings Bay Site

A conceptual model of the Kings Bay site, in southeastern Georgia, was developed from drilling logs and long-term monitoring data (fig. 10). The sediments underlying the site are of marginal marine origin and reflect the progradation of the shoreline over geologic time. Sediments exposed at land surface consist of fine- to medium-grained sands of wind-blown dune (aeolian) origin and range from 2 to 3 meters in thickness. Below these surface sands is a layer of organic-matter-rich sands and clays that record sedimentation in a back-bay lagoon environment. This organic-matter-rich layer is typically 3 meters thick and is areally extensive in the vicinity of the site. A photograph of this unit in outcrop, taken 2 miles from the site is shown in figure 5. Underlying the layer of organic-matter-rich sediments is another layer of fine- to medium-grained aeolian sand that ranges from 5 to 7 meters thick. This sandy layer is underlain by clayey sediments of marginal marine origin.

The hydrology of this site reflects the interaction of these geologic units. The sands exposed at land surface are relatively permeable and absorb most of the atmospheric precipitation that falls on the site. During precipitation, water saturates the sandy soil and percolates downward into the subsurface. For the first 2 or 3 meters of vertical flow, percolating recharge encounters soils and fine-grained quartz sands until it reaches the water table. The depth to the water table varies as much as 1 to 2 meters, depending on the amount of recent rainfall. Typically, the water table resides in the sandy surface sediments above the organic-matter-rich layer. The organic-matter-rich layer is characterized by a lower hydraulic conductivity than the surface sands, but during and after rainfall, water moves downward through the organic-matter-rich layer, recharging the semiconfined aquifer beneath. The semiconfined aquifer has a higher hydraulic conductivity than the overlying organic-matter-rich layer, and ground-water flow changes from being predominantly vertical (in the organic-matter-rich layer) to horizontal (in the semiconfined layer). The semiconfined aquifer, therefore, acts as a regional "drain" moving recharge water from topographic highs near the landfill to discharge areas to the west (fig. 10).

During operation of the landfill (1978–1985), trenches were dug to a depth of about 8 feet, filled with municipal waste, and covered. Traces of these trenches are still visible at land surface (fig. 10). At some time during landfill operation, PCE, probably waste from a dry-cleaning operation, was disposed of in the trenches. The relatively dense PCE moved downward through the soil, the organic-matter-rich confining bed, and the semiconfined aquifer, finally pooling on the underlying confining bed. Horizontally flowing ground water dissolved the PCE, carrying it downgradient in the direction of a nearby housing subdivision. Because of the ambient anoxic conditions present in the semiconfined aquifer, PCE was subject to reductive dechlorination, transforming it to TCE, DCE, and VC. Each of these contaminants was subject to natural attenuation processes including advection, dispersion, sorption, and biodegradation, which tended to restrict expansion of the plume. In 1998, a series of observation wells were installed to delineate the areal extent of the plume (fig. 11). At that time, VC was observed 100 meters downgradient of the contaminant source area and impacted the nearby subdivision. Concentrations of chlorinated ethenes along the axis of the plume show that PCE and TCE predominated near the source area, and they were transformed to DCE and VC along the flowpath (fig. 12). Importantly, the VC concentration was observed to drop below detectable levels at the most downgradient well (KBA-11-37) although DCE was still detectable.

The observed patterns of chlorinated ethene biodegradation in the semiconfined aquifer reflects the redox chemistry of the site (fig. 13). Ground water in the semiconfined aquifer, including ground water outside of the contaminant plume, is predominantly anoxic, and contains moderate concentrations of ferrous iron [Fe(II)], sulfide, and methane. This chemistry reflects the transport of recharge water through the organic-matter-rich confining bed (fig. 10), consumption of dissolved oxygen by aerobic microorganisms, and the establishment of

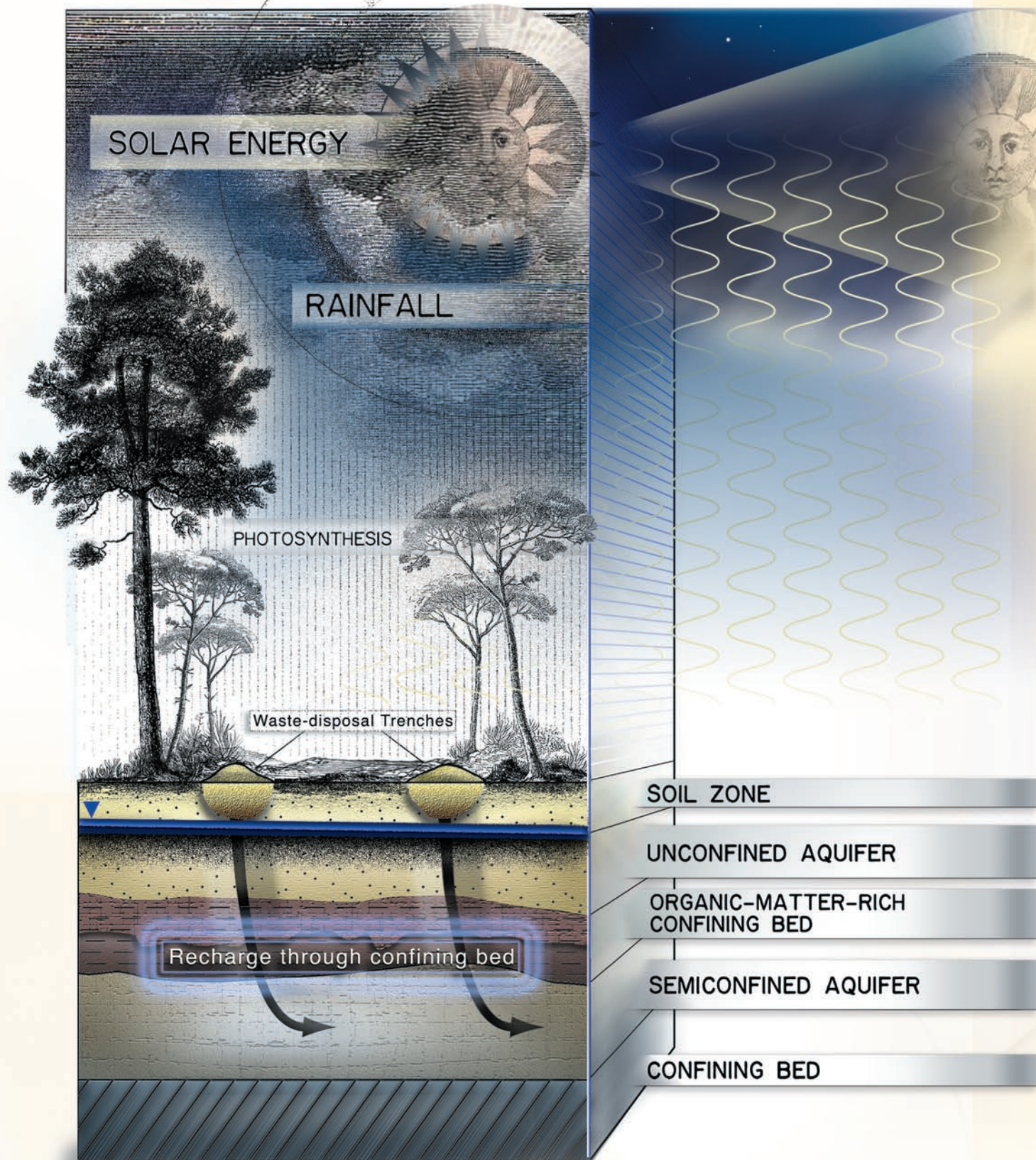


Figure 10. Conceptual model of the Kings Bay site in southeastern Georgia.

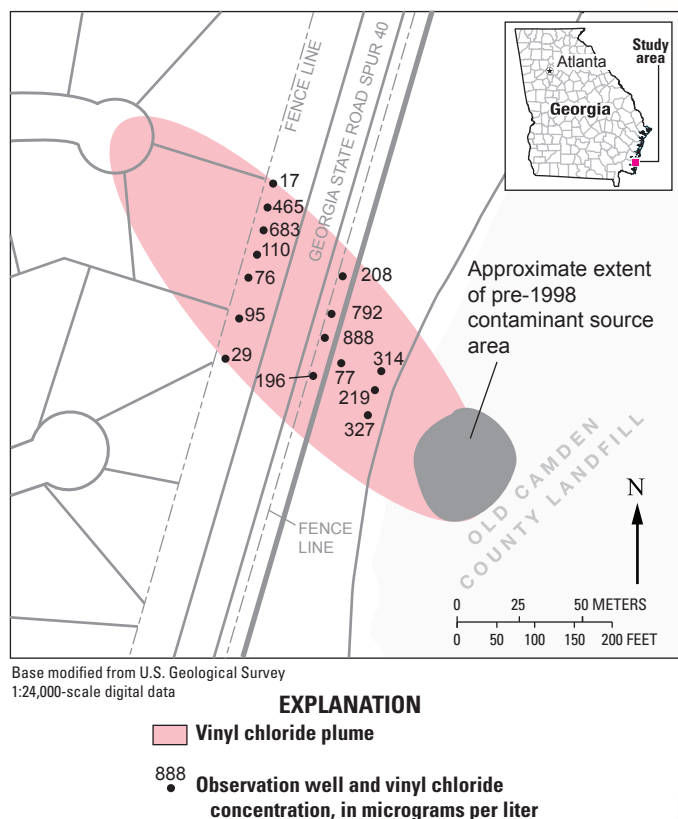


Figure 11. Concentrations of vinyl chloride in the Kings Bay, Georgia, plume, November 1998.

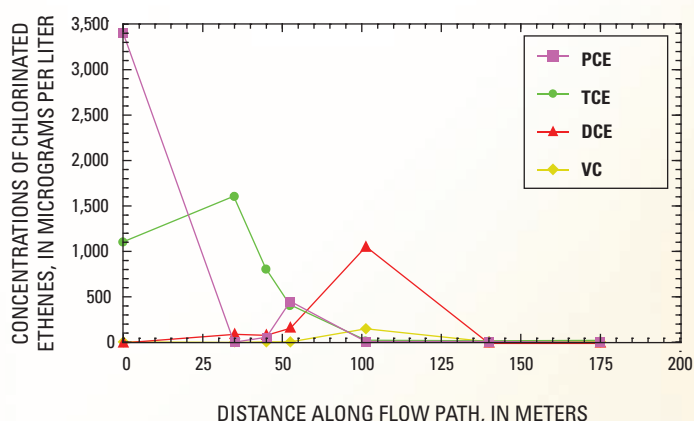


Figure 12. Concentrations of chlorinated ethenes along the flowpath of the Kings Bay plume.

anoxic conditions. Observed concentrations of dissolved iron and sulfide, as well as concentrations of hydrogen in the 0.3 to 2.0 nanomoles per liter (nM/L) range (fig. 13), indicate predominantly sulfate-reducing and Fe(III)-reducing conditions in the semiconfined aquifer. The observed increase in methane concentrations may reflect methane generation in the organic-matter-rich semiconfined layer rather than active methanogenesis in the semiconfined aquifer itself. Near the landfill, sulfate-reducing conditions appear to predominate, and as ground water flows downgradient, Fe(III) reduction becomes increasingly predominant in the semiconfined aquifer.

The sulfate-reducing conditions near the source area facilitate the initial reduction of PCE and TCE to DCE and VC (fig. 12). Farther downgradient, however, the lack of measurable ethene concentrations in ground water suggests a net mineralization of DCE and VC. One possibility for this difference is that VC is reduced to ethene, which then mineralizes under anoxic conditions to CO_2 . Another possible explanation is that VC is directly mineralized to CO_2 with no intermediate reductive step. Because VC is less likely than DCE to undergo reduction, because VC is absent from the most downgradient ground water, and because DCE is present at low concentrations (about 10 micrograms per liter [$\mu\text{g/L}$]) in downgradient ground water, anoxic mineralization of VC is a possible mechanism at this site.

Constructing the Deterministic Model

The conceptual model of the Kings Bay site described previously (fig. 10) was used to construct a deterministic model of the site for the purpose of quantifying the mass and energy balance over time. The goals of this exercise included:

1. Quantifying the flux of electron donors and acceptors, including chlorinated ethenes, to the semiconfined aquifer and evaluating how this flux affects redox conditions and biodegradation processes.
2. Estimating the time required for the NAPL source to dissolve and disperse, eliminating the contaminant plume. This provides an estimate of how long the plume can be expected to persist, and thus the length of time natural attenuation processes will need to be sustained into the future.
3. Quantifying the flux of dissolved organic carbon to the semiconfined aquifer, quantifying the mass of renewable (soil zone) and nonrenewable (organic-matter-rich confining bed) sources of organic carbon in order to assess the long-term sustainability of natural attenuation at this site.

The deterministic mass- and energy-balance model was built in three steps. First, estimates of parameters describing the geologic, hydrologic, and microbiologic conditions of the site were estimated and entered as initial input to the model. Secondly, these model parameters were constrained to reproduce observed rates of ground-water flow and observed redox conditions at the site. Thirdly, the mass of NAPL present in the semiconfined aquifer was constrained by comparing observed and simulated concentrations of dissolved chloride,

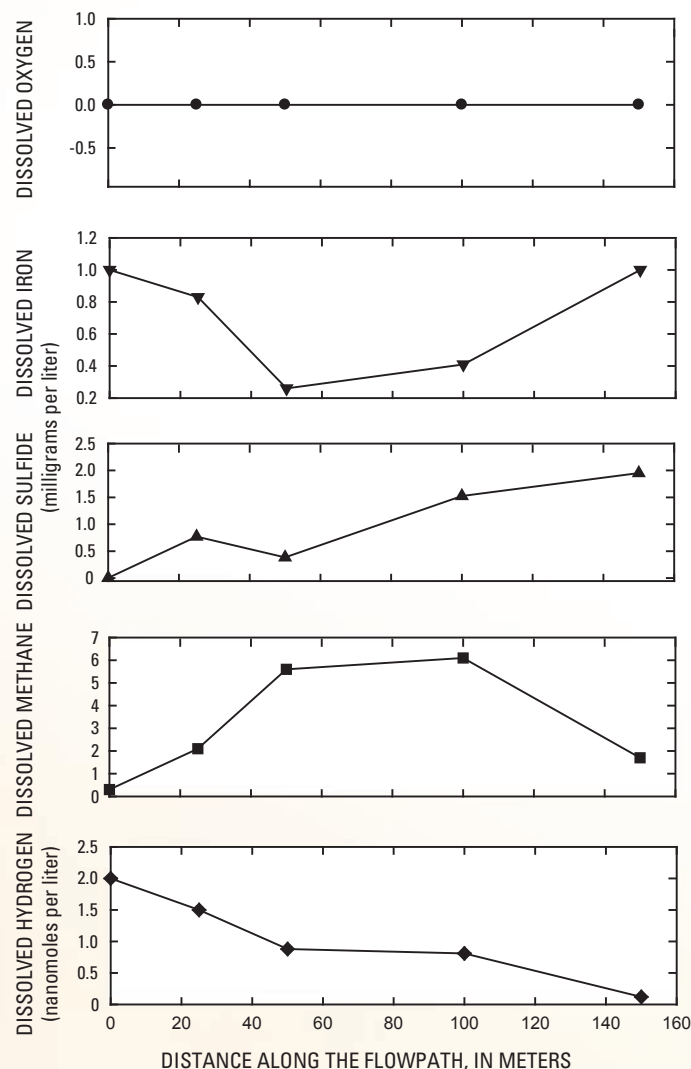


Figure 13. Concentrations of redox indicator parameters along the flowpath of the Kings Bay plume.

the final degradation product of chloroethene transformation. Finally, rates of dissolved chlorinated ethene biotransformation were constrained by comparing observed and simulated concentrations of dissolved PCE, TCE, DCE, and VC.

The boundary conditions, hydrologic parameters, NAPL dissolution parameters, geochemical, redox, and microbial population parameters, and chlorinated ethene biodegradation parameters used in the SEAM3D simulations of this system are provided in Appendix 2.

Constraining the Mass-Balance Model

The large number of hydrologic, microbiologic, and geochemical parameters needed for the coupled set of mass-balance equations (Appendixes 1 and 2) solved by the SEAM3D code presents a significant challenge. Specifically, the parameter values must be adjusted so that the model gives

a realistic representation of the natural system. The large number of parameters involved makes it impossible to select a unique combination of parameters that describe the system. Given this challenge, the approach taken in this report was to constrain the parameter values using available hydrologic, microbiologic, and geochemical field data. The model was constrained in four steps:

1. Given observed water levels and aquifer-test estimates of hydraulic conductivity and porosity, the MODFLOW portion of the code was used to simulate rates of ground-water flow. Simulated rates of ground-water flow were then compared to observed rates of sulfate transport from a Fenton's Reagent injection monitored for 6 years. The hydraulic conductivity and porosity values specified in the model were chosen to reproduce observed rates of ground-water flow.
2. The mass of NAPL in the contaminant source area initially was estimated by considering how much PCE might have been disposed of at the site. These estimates were refined by considering the observed distance of PCE transport downgradient from the source area, the distribution of chlorinated ethene daughter products, and observed concentrations of dissolved chloride produced from within the source area.
3. The areal recharge to the semiconfined aquifer was constrained by comparing the observed and simulated dilution of the chloride plume as it is transported downgradient from the source area.
4. The transport of dissolved oxygen and organic carbon substrate to the semiconfined aquifer was constrained by comparing observed and simulated distribution of redox conditions, and by comparing observed and simulated concentrations of dissolved organic carbon.

Rates of Ground-Water Flow

The first step in obtaining a realistic mass balance of a ground-water system is to have an accurate estimate of ground-water flow rates. These estimates are obtained by solving the ground-water flow equation for appropriate boundary and initial conditions, and then applying Darcy's equation to obtain ground-water velocity. In the SEAM3D code, these calculations are made by using the MODFLOW ground-water flow model. The hydrologic parameters used to simulate ground-water flow at this site are provided in Appendix 2. Initial estimates of these parameters were made from aquifer tests conducted at the site (Leeth, 1999), and were adjusted so that the observed head distribution at the site was reproduced by MODFLOW simulation. The observed head distribution could be simulated by using constant-head nodes at the upgradient and downgradient boundaries to simulate lateral flow into and out of the system, assuming an areally constant value for hydraulic conductivity, and assuming a constant flux

of vertical recharge to the aquifer from rainfall. While these hydrologic parameters yield a simulated head distribution that closely matched the observed head distribution, it does not follow that the simulated flux of water is representative of the system.

One way to constrain ground-water flow rates simulated by the model, which have a large affect on the simulated mass balance of the system, is to compare simulated and observed transport rates of a solute through the system. Because Fenton's Reagent, a mixture of ferrous sulfate and hydrogen peroxide, was injected into the source area of this site in 1998, the transport of sulfate downgradient provides an estimate of ground-water travel time in the aquifer. Sulfate, which is subject to retardation, is not the ideal solute for this approach. Nevertheless, the observed breakthrough of sulfate in the downgradient wells can be used to constrain the simulated

flux of water through the model if sorption is considered. The breakthrough of sulfate at well KBA-11-13A, which occurred approximately 1.5 years after the injection, indicates a sulfate velocity of about 15 meters per year (fig. 14). The transport of a tracer, with a sorption coefficient appropriate for sulfate, was simulated with the model, and a hydraulic conductivity needed to match the observed sulfate velocity was identified (Appendix 2). The model, therefore, simulates a ground-water velocity comparable to what is observed in the field.

In addition to helping constrain rates of ground-water flow at the site, the arrival of Fenton's Reagent-treated high-concentration sulfate water at well KBA-11-13A coincided with large declines in chlorinated ethene concentrations (fig. 14). This, in turn, shows that the Fenton's Reagent treatment was effective in lowering contaminant concentrations at the source area.

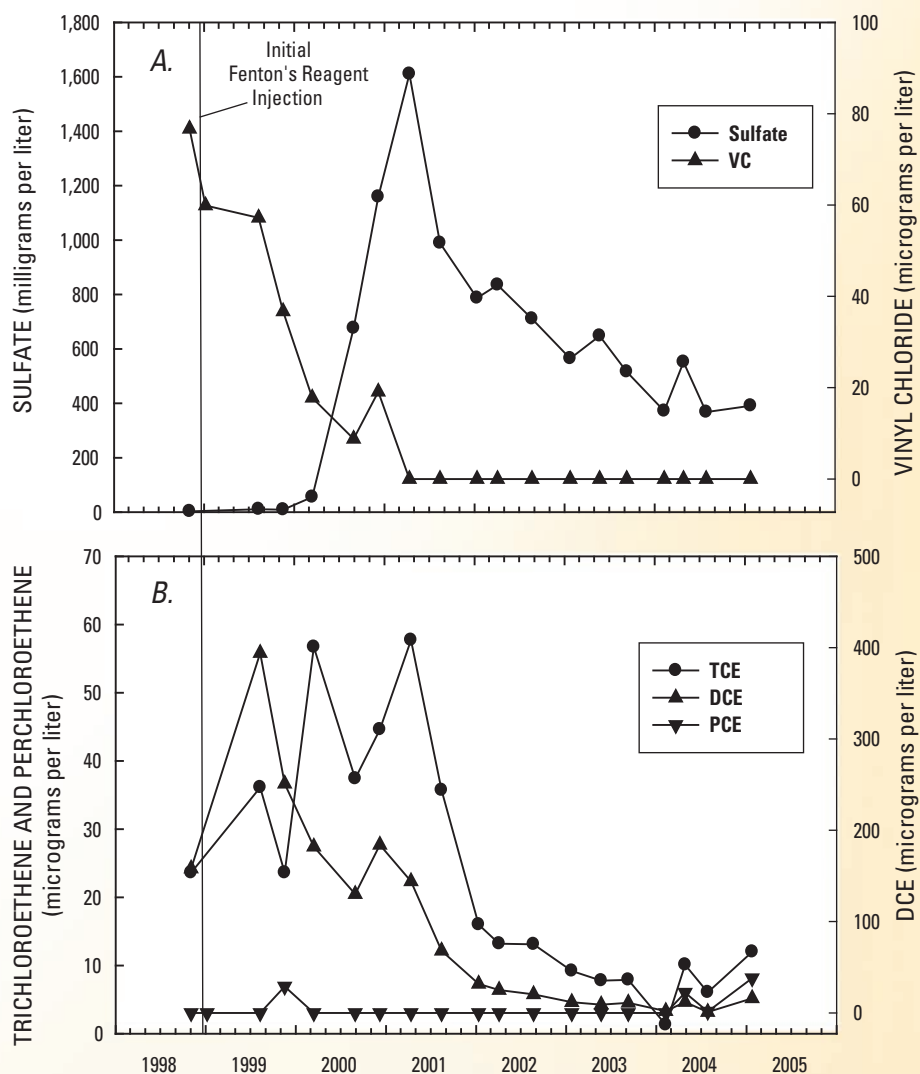
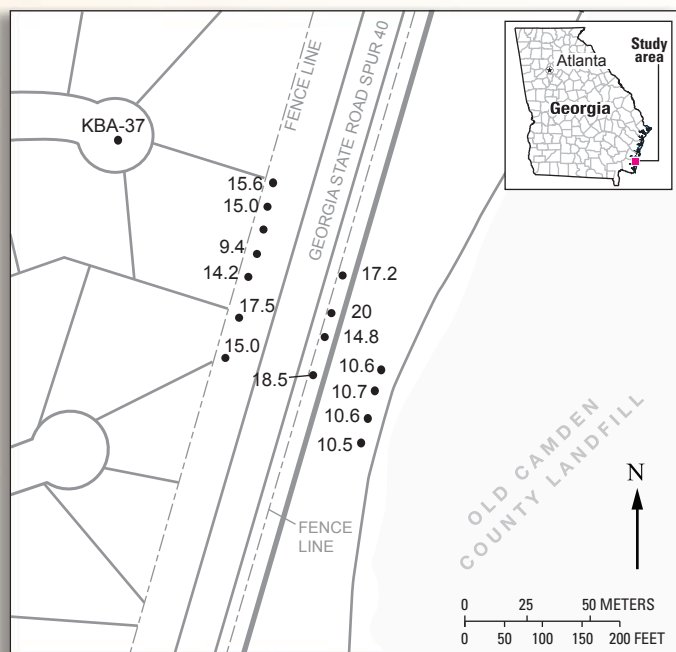


Figure 14. Concentration changes of (A) sulfate and (B) chlorinated ethenes over time at well KBA-11-13A from 1998 through 2004.

Areal Recharge to the Semiconfined Aquifer

The amount of areal recharge to the semiconfined aquifer was constrained by observed concentration changes of dissolved chloride in the plume. Near the contaminant source area at the first line of USGS observation wells, where chloroethene biodegradation is relatively incomplete, average chloride concentrations were 10.6 mg/L (fig. 15). Chloride concentrations increase at the second line of wells (to the west) to an average of 17.6 mg/L, reflecting the biotransformation of chlorinated ethenes. Significantly, chloride concentrations decrease slightly at the third line of wells to an average of 14.5 mg/L. Model simulations that did not include areal recharge through the semiconfining bed indicated that chloride concentrations would continue to increase between the second and third line of wells. When areal recharge of low-chloride water to the aquifer was included, the observed downgradient dilution of the chloride plume could be reproduced. An areally constant value of recharge to the aquifer of 0.001 meter per day (m/d) per model cell (1 liter per day per 25 square meters [$L/d/25\text{ m}^2$]) captured the observed downgradient dilution of the chloride plume.



Base modified from U.S. Geological Survey
1:24,000-scale digital data

EXPLANATION

- 10.5 Observation well and chloride concentration, in milligrams per liter
- KBA-37 Monitoring well and number

Figure 15. Observed chloride concentrations in ground water at the Kings Bay site, November 1998.

Mass Balance of NAPL

The NAPL Dissolution Package of SEAM3D was used to simulate the dissolution of NAPL present at the site (Appendixes 1 and 2). Several lines of evidence were used to refine NAPL mass estimates. First, the distance that PCE was observed to move downgradient from the source area was captured over time at well KBA-11-13A. PCE was observed to reach well KBA-11-13A by the early 1980s at concentrations of about 20 $\mu\text{g/L}$, but by 1998, the PCE plume had regressed slightly back toward the source area (Southern Division, Naval Facilities Engineering Command, 2004). These data indicate that the dissolution of PCE over time has decreased and the size of the PCE plume was shrinking by 1998. The amount of NAPL placed in the modeled source area was constrained to reproduce the observed initial transport of PCE to well KBA-11-13A after 20 years of simulation, and to reproduce the subsequent recession of the PCE plume from that well.

Another line of evidence available to constrain the mass of NAPL initially present in the source area is observed concentrations of chloride near the source area. Since chloride is a final product of chloroethene degradation, the amount of chloride delivered to ground water is proportional to the mass of PCE dissolving and being transformed. At the Kings Bay site in 1998, observed concentrations of chloride at the first (most eastern) line of observation wells (near the plume source area) averaged 10.6 mg/L. At the second line of observation wells, chloride concentrations increased to 17.6 mg/L, reflecting the overall biodegradation of chlorinated ethenes (fig. 15). The final step in constraining the amount of NAPL present in the source area was to adjust the parameters to reproduce the observed chloride plume.

The mode of landfill operation suggests that between one and ten 55-gallon barrels of NAPL were released at the site. Table 1 shows the sensitivity of simulated chloride concentrations at the second line of wells to different assumed masses of NAPL. When two-thirds of a 55-gallon barrel of

Table 1. Observed sensitivity of simulated chloride concentrations to a non-aqueous phase liquid (NAPL) mass.

[kg, kilogram; g/g, gram per gram; mg/L, milligrams per liter]

Simulated NAPL mass in each of three source area model cells (kg)	Simulated NAPL mass in each of three source area model cells (g/g) ¹	Simulated chloride concentration increase at the second line of observation wells (mg/L)
477	0.010	9
373	0.008	8
187	0.004	7
94	0.002	6

¹Assumes cell volume of 25 cubic meters.

PCE (187 kg) was simulated in each of the three source area model cells ($C^N = 0.004$ g/g), the resulting increase in chloride was approximately 7 mg/L.

For a specified C^N (NAPL mass in grams of NAPL per gram of sediment) of 0.008 g/g, the simulated chloride increase was 8 mg/L, and for a C^N of 0.010 g/g, the chloride concentration increase was 9 mg/L. Because the observed increase in chloride concentration was approximately 8 mg/L, a value of 0.008 g/g was assigned to each source area node in the constrained model. This simulated NAPL mass is equivalent to about four 55-gallon barrels of PCE in the source area. This was simulated by assigning a NAPL mass of 373 kg of PCE to each of three source-area model cells. Because of the uncertainty associated with NAPL mass, however, simulations designed to estimate times of remediation used a range of NAPL estimates.

Mass Balance of Electron Donors and Acceptors

SEAM3D is designed specifically to track the sequential utilization of electron acceptors in ground-water systems. The code uses inhibition functions (Appendix 1) to specify the sequential utilization of electron acceptors in the order oxygen > chlorinated ethenes > Fe(III) > sulfate > carbon dioxide coupled to the oxidation of dissolved organic carbon. If dissolved oxygen is available (greater than 1 mg/L), the oxidation of organic carbon is coupled stoichiometrically to oxygen reduction. SEAM3D also considers solid ferric oxyhydroxides present in aquifer sediments as an electron acceptor. Thus, once oxygen has been consumed, oxidation of organic carbon is coupled to solid ferric hydroxides. The product of this reaction, dissolved ferrous iron [Fe(II)], is then tracked as a solute. Once solid ferric hydroxides have been depleted, oxidation of organic carbon switches to sulfate, and finally to carbon dioxide (fig. 8). These features enable the user to simulate electron flow between electron donors (organic carbon) and available electron acceptors, and thus, to quantify the energy balance of a system.

SEAM3D simulations then were used to evaluate the energy balance for the Kings Bay site. Once estimates for the amount of areal recharge entering the aquifer were constrained by the observed dilution of chloride along the flowpath, different concentrations of dissolved organic carbon were assigned to vertically percolating recharge, simulating the transport of carbon from the soil zone and the organic-matter-rich beds overlying the aquifer. In addition, recharging water was specified to contain various concentrations of electron acceptors in order to simulate the distribution of energy between available electron acceptors. Concentrations of solid ferric hydroxides present in the aquifer matrix were varied between 50 and 100 micrograms per gram ($\mu\text{g/g}$). The model was constrained by reproducing the observed distribution of redox processes at the site. This included simulated dissolved oxygen concentrations less than 0.2 mg/L, sulfate-reducing conditions near the landfill grading to Fe(III)-reducing conditions downgradient, and dissolved organic carbon concentrations of approximately 2 mg/L.

Mass Balance of Dissolved Chlorinated Ethenes

The last step in constraining the mass-balance model was to adjust the Monod kinetic parameters for reductive dechlorination of chlorinated ethenes, and the direct oxidation of VC, in order to reproduce the observed 1998 concentrations of dissolved chlorinated ethenes. This was done on a trial and error basis, and began with comparing the observed and simulated distribution of the PCE plume near the source area. Once the PCE plume was adequately reproduced, attention turned to the TCE plume, then to DCE, and finally to VC. The most difficult part of this procedure was to reproduce the observed behavior of the DCE and VC plumes. Monitoring data show that the DCE plume extended farther downgradient than the VC plume. This observed pattern could not be reproduced by considering reductive dechlorination to be the only ongoing biodegradation process. Because VC is produced from DCE by reductive dechlorination, it was not possible to adjust the parameters so that the DCE plume was longer than the VC plume. Microcosm experiments conducted with aquifer material from the Kings Bay site indicate that VC is subject to a combination of reductive dechlorination and anoxic mineralization (Bradley, 2003). For this reason, kinetic parameters for the anoxic mineralization of VC were included in the model. This, in turn, allowed the reproduction of the observed DCE and VC plume configurations. The final simulated and observed 1998 distributions of PCE, TCE, DCE, and VC are shown in figure 16.

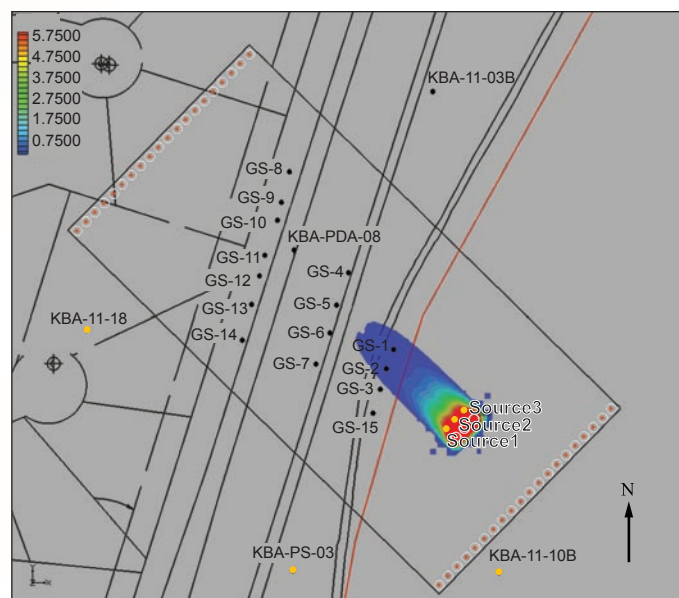
Assessing the Sustainability of Natural Attenuation

After the model was constrained, SEAM3D was used to assess the sustainability of natural attenuation at the Kings Bay site. This sustainability depends upon the mass balance between contaminant loading and attenuation, the delivery of dissolved organic carbon needed to transform the contaminants, and the sequestration of energy from organic carbon between competing electron-accepting processes. These issues of mass and energy balance can be quantitatively assessed using the deterministic model.

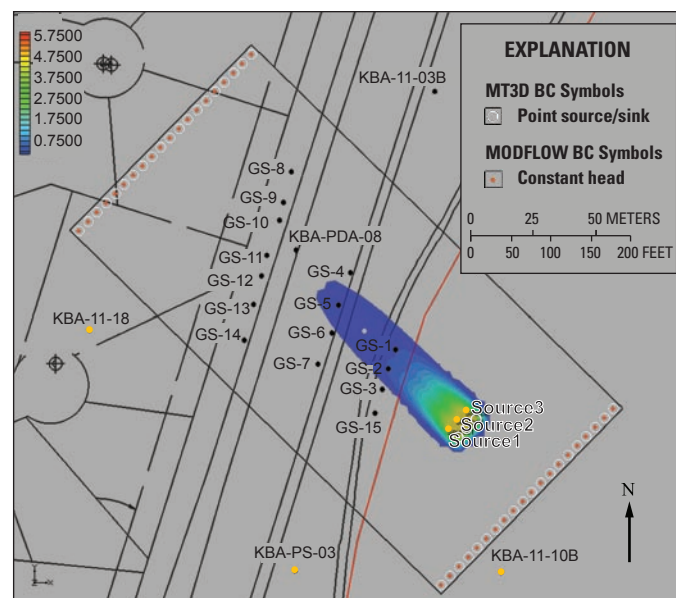
One approach for assessing sustainability is to use the model to illustrate how possible future changes in site conditions may affect contaminant behavior. This approach utilizes the time-dependent nature of the mass and energy balance equations that comprise the model, and can suggest ways of managing the site over time so as to maximize the sustainability of natural attenuation. The sustainability of MNA at the Kings Bay site was assessed in several ways.

1. The dissolution of NAPL and the size of the resulting chlorinated ethene plume were simulated over time to estimate the length of time needed for natural processes to deplete the contaminant source and remediate the plume. This, in turn, provided an estimate of the time frame over which natural attenuation processes would need to be sustained.

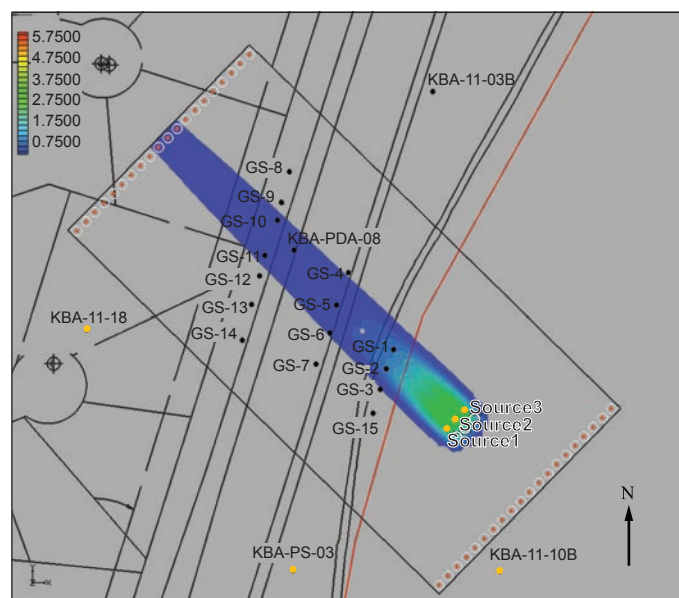
PCE



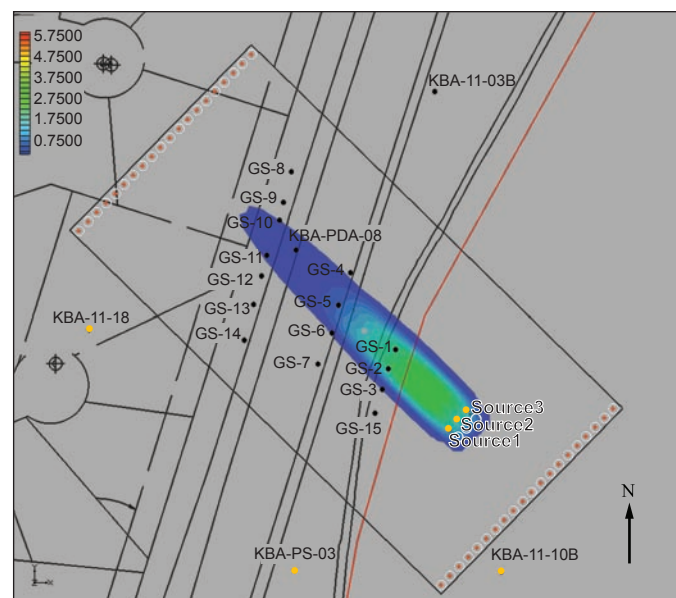
TCE



DCE



VC



Base modified from U.S. Geological Survey
1:24,000-scale digital data

Figure 16. Simulated and observed 1998 concentrations of chlorinated ethenes.

2. The removal of the NAPL source was simulated to estimate the length of time needed for the contaminant plume to degrade once its source was gone. This provided estimates of the minimum time frame over which natural attenuation processes would need to be sustained.
3. The flux of dissolved oxygen and dissolved organic carbon to the aquifer was varied to estimate the minimum delivery of organic carbon needed to sustain reductive dechlorination over time.
4. The minimum flux of dissolved organic carbon required to sustain reductive dechlorination was compared to renewable and nonrenewable sources of organic carbon to assess the long-term sustainability of MNA at the site.
5. The effects of ferric oxyhydroxide concentrations in aquifer sediments on the sustainability of VC-degrading processes over time.

NAPL Dissolution and Time of Remediation

Assessing the sustainability of MNA requires an estimate of how long reductive chlorination processes will need to be sustained over time. One way to estimate this is to consider the length of time needed for a NAPL source to dissolve and for the resulting plume to disperse. Simulations allowing the estimated mass of NAPL present in the system, as constrained by available hydrologic and geochemical data, were performed in order to make these estimates. Because the mass of NAPL emplaced in the aquifer is subject to uncertainty, a range of NAPL masses were simulated in each of three source-area cells ranging from 187 kg (two-thirds of a 55-gallon barrel) to 467 kg (one and two-thirds of a 55-gallon barrel). For these simulations, the time of remediation (TOR) was defined when concentrations of VC dropped below 5 µg/L throughout the model domain. The results of these simulations are summarized in table 2.

The estimated TORs from these simulations ranged from a minimum of 100 years to more than 500 years. These results indicate that TOR at this site—assuming that the NAPL is left in place and allowed to dissolve over time—will be greater than 100 years. Thus, in the absence of engineered NAPL removal actions, it is reasonable to conclude that MNA will have to be sustained at this site for approximately 300 years.

NAPL Removal and Time of Remediation

Guidance from the U.S. Environmental Protection Agency (1999) states that “monitored natural attenuation can be selected as a remediation alternative when the timeframe is reasonable compared to other remediation technologies.” The Georgia Department of Environmental Protection, the State agency responsible for environmental regulation at the Kings Bay site, concluded that any remedial strategy that would take longer than 50 years was not “reasonable” and could not be accepted. As a result, the U.S. Navy began considering other strategies for remediating the Kings Bay site. The technology selected was in situ oxidation using Fenton’s Reagent injection. Accordingly, in December 1998, a series of Fenton’s Reagent injections were performed and a monitoring program

Table 2. Estimated times of remediation for different non-aqueous phase liquid (NAPL) masses.

[kg, kilogram; g/g, gram per gram; >, greater than]

Simulated NAPL mass in each of three source area model cells (kg)	Simulated NAPL mass in each of three source area model cells (g/g) ¹	Estimated time of remediation (years)
467	0.010	>500
373	0.008	500
280	0.006	160
187	0.004	100

¹Assumes cell volume of 25 cubic meters.

was initiated to assess the behavior of the contaminant plume after treatment with Fenton’s Reagent.

The waste-removal action was simulated in SEAM3D by instantly removing the NAPL after 20 years of simulation (at 1998) and simulating the subsequent collapse of the contaminant plume. Because monitoring data following source area removal are available at this site, it is possible to compare simulated and measured chloroethene concentrations. Simulated and measured VC concentrations for 2004, which are shown for comparison in figure 17, are generally similar. The model was then used to simulate the length of time needed for VC concentrations to decline below 2 µg/L throughout the plume. Based on this approach, the estimated time of remediation was approximately 14 years following Fenton’s Reagent treatment which corresponds to the year 2012.

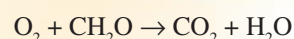
These two TOR estimates—for the case of no NAPL removal and for the case of NAPL removal—indicate that natural attenuation processes would need to be sustained for at least 100 years if NAPL were not removed, and approximately 14 years if the NAPL were removed. In practice, the option to not remove the NAPL is moot since Fenton’s Reagent treatment has already occurred. Nevertheless, the model can be used to illustrate how different environmental conditions may affect the sustainability of MNA in this system.

Dissolved Oxygen/Dissolved Organic Carbon Flux: Short-Term Sustainability

Qualitatively, the sustained reductive dechlorination of chlorinated ethenes depends upon the establishment of anoxic conditions, at least to Fe(III) reduction, allowing part of the electron flow to be captured by chlororespiration (fig. 8). The SEAM3D model described in this report can be used to illustrate how the interaction of dissolved oxygen and dissolved organic carbon present in recharging ground water affects the establishment of anoxic conditions.

The conceptual model of the Kings Bay site (fig. 10) assumes that dissolved oxygen and dissolved organic carbon are delivered to the semiconfined aquifer by areal recharge. The actual delivered concentrations of these species, however, is uncertain. By varying the concentrations of dissolved oxygen and organic carbon being delivered to the aquifer in the SEAM3D model, it is possible to illustrate the effects of these species on redox conditions and chlorinated ethene biodegradation in the system.

During the model-constraining procedure, the most realistic comparison between simulated and measured redox conditions and chlorinated ethene biodegradation was achieved using concentrations of 5 mg/L dissolved oxygen [0.156 millimoles per liter (mM/L)] and 5 mg/L dissolved organic carbon (0.167 mM/L) in recharging water, which reflect the stoichiometry of oxygen consumption



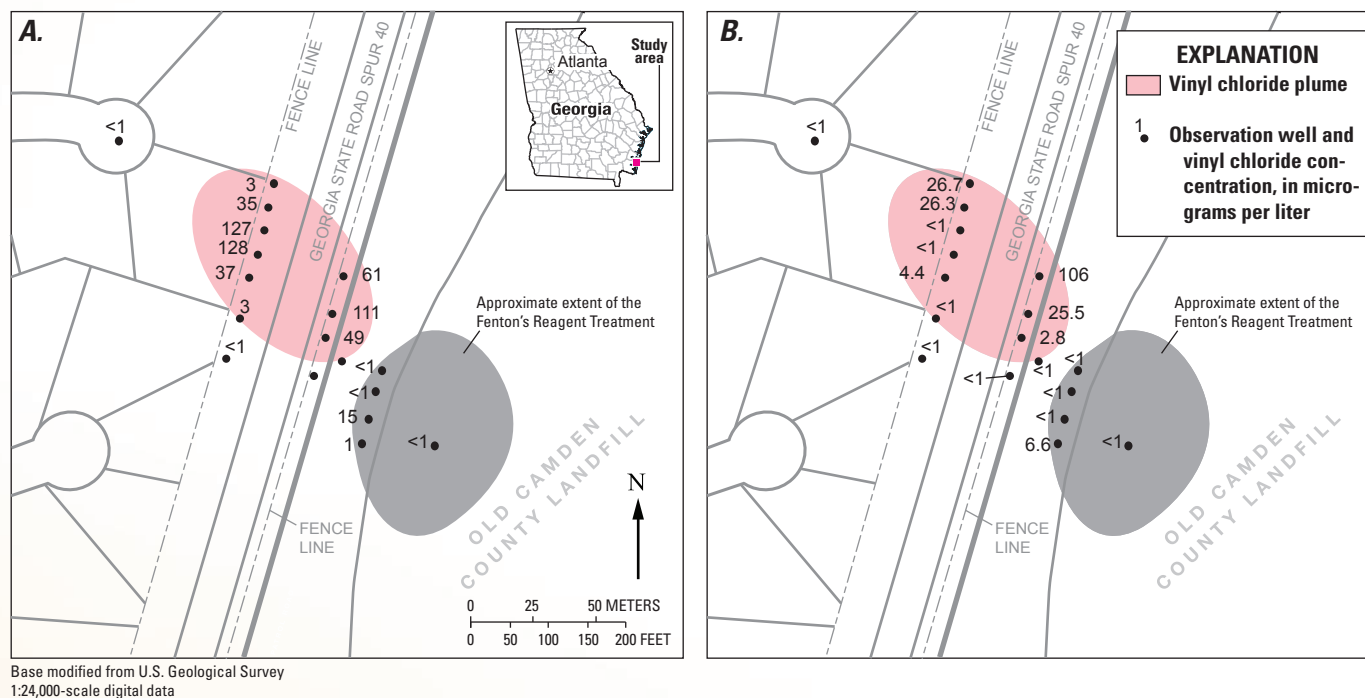


Figure 17. The (A) simulated and (B) measured 2004 concentrations of chlorinated ethenes following source-area removal in 1998.

and the slightly greater molar concentration of dissolved organic carbon relative to oxygen. The short-term requirement for the sustainability of MNA for chlorinated ethenes is that the molar ratio of dissolved oxygen (DO) to organic carbon (both dissolved and particulate; DOC) delivered to the aquifer be less than 1. As a result,

$$\text{STSR (dimensionless)} = \frac{\text{DO (mol/L)}}{\text{DOC (mol/L)}} < 1, \quad (4)$$

where STSR may be called the “short-term sustainability ratio” and concentrations of DO and DOC are expressed in molar units. When STSR is less than 1, anoxic conditions develop and the flow of energy proceeds toward the biodegradation of chlorinated ethenes. Conversely, when STSR is greater than 1, oxic conditions develop and the flow of energy is diverted away from chloroethene biodegradation.

The effects of the dissolved oxygen/dissolved organic carbon (DO/DOC) ratio on the sustainability of MNA at Kings Bay can be illustrated using model simulations. When the DO/DOC ratio (in units of milligrams per liter) in areal recharge was low (1/5 mg/L), then redox conditions were more reducing and the size of the simulated PCE plume was correspondingly small (fig. 18), reflecting active chlororespiration. When the DO/DOC ratio was increased to 5/5, conditions remained anoxic, but more electron flow was sequestered by sulfate and Fe(III) reduction relative to chlororespiration and the simulated size of the PCE plume increased. When oxic conditions were established by simulating a DO/DOC ratio of 5/1, simulated

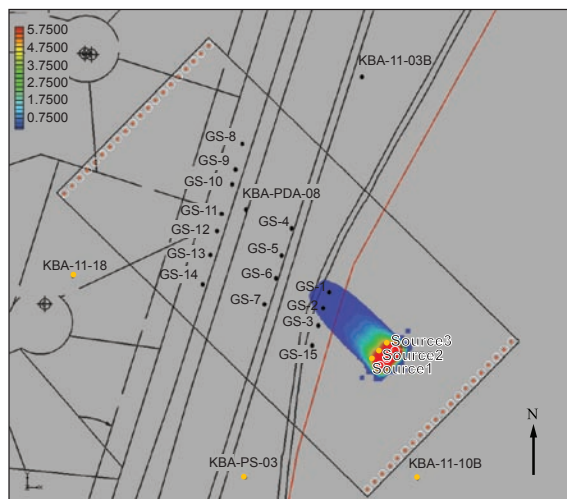
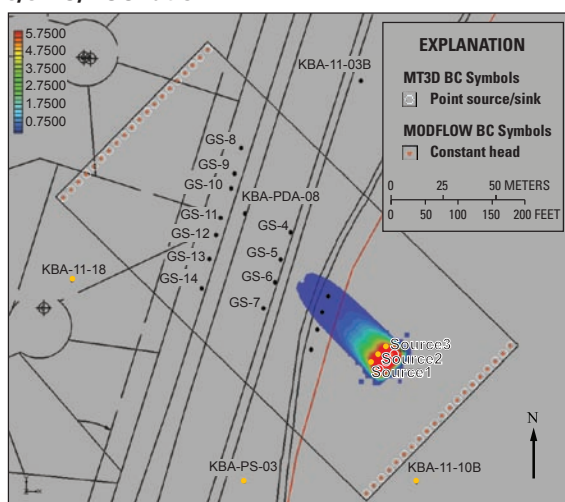
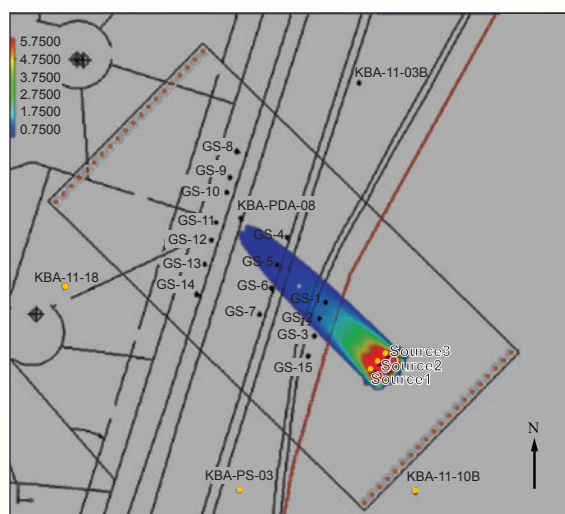
DOC concentrations declined below 1 mg/L. This further decreased the energy flow toward chlororespiration and caused the size of the simulated PCE plume to expand (fig. 18).

The most basic, short-term requirement for sustaining MNA for chlorinated ethenes, therefore, is that the molar flux of organic carbon to a system exceeds the molar flux of dissolved oxygen. At the Kings Bay site, this requirement for the short-term sustainability of MNA is met.

Available Organic Carbon and Dissolved Organic Carbon Flux: Long-Term Sustainability

Given estimates of DOC flux to the semiconfined aquifer, a flux sufficient to maintain short-term MNA for chlorinated ethenes, it becomes possible to address the long-term sustainability of MNA as well. Qualitatively, if the amount of available organic carbon (AOC) present in the system is large relative to the flux of DOC needed to sustain anoxic conditions, then MNA will be more sustainable in the long term. Conversely, if the amount of AOC is small relative to the DOC flux, then MNA will be less sustainable. The results of the SEAM3D simulations, which give estimates of the DOC flux, make it possible to evaluate the ratio between DOC flux and AOC.

For each model grid block (5 m x 5 m), the areal recharge rate is 0.001 m/d (1 L/d). Assuming this recharge contains 5 mg/L of dissolved organic carbon, the DOC flux to the aquifer from each model cell is 5 mg/d. This flux can be compared to the pool of organic carbon present in the soil zone and organic-matter-rich confining bed overlying the aquifer (fig. 10).

1/5 DO/DOC ratio**5/5 DO/DOC ratio****5/1 DO/DOC ratio**

Base modified from U.S. Geological Survey
1:24,000-scale digital data

Figure 18. Simulated 1998 PCE concentrations for DO/DOC ratios of 1/5, 5/5, and 5/1. All ratios are in milligrams per liter.

The most basic measure of the organic carbon content of soils and sediments is weight loss on ignition (LOI). Because much of the combustible organic carbon indicated by LOI is not bioavailable, however, it is not an appropriate measure of available organic carbon. Methods for directly measuring organic carbon content and extractable bioavailable organic carbon are available (Rectanus and others, 2005); these methods were used to estimate AOC at the Kings Bay site. The results of these analyses indicate considerable variability in the amount of organic carbon present (table 3). In general, soil-zone sediments have the least amount of organic carbon, and the organic-matter-rich confining bed has the most. These estimates for the amount of extractable bioavailable organic carbon present in the sediments overlying the semiconfined aquifer make it possible to evaluate the ratio of DOC flux to the amount of AOC.

The 2-m thickness of sandy soil and sediments at land surface (fig. 10) has a bioavailable organic carbon content of approximately 500 mg/kg (table 3). Given the volume of each model grid block (5 m x 5 m x 2 m) and a bulk density of $1.85 \times 10^3 \text{ kg/m}^3$, the resulting sediment mass in each block is $9.3 \times 10^4 \text{ kg}$. Furthermore, given the measured concentration of bioavailable organic carbon in the sediment (500 mg/kg), the sediment contains on the order of $4.7 \times 10^7 \text{ mg}$ of potentially metabolizable organic carbon. The 3-meter-thick organic-matter-rich confining bed overlying the aquifer can be treated in the same manner. Given a grid block volume of 5 m x 5 m x 3 m and a measured concentration of bioavailable organic matter of 5,000 mg/kg, the resulting mass of potentially metabolizable organic carbon is $6.9 \times 10^8 \text{ mg}$. In other words, the organic-matter-rich confining bed contains approximately an order of magnitude more bioavailable organic carbon than the soil zone. The sum of potentially available organic carbon in the soil zone and in the organic-matter-rich confining bed at the Kings Bay site is on the order of $7.4 \times 10^8 \text{ mg}$ per 125 m^3 , or $5.9 \times 10^6 \text{ mg/m}^3$.

If it is assumed that DOC is continually delivered to the aquifer by vertically percolating recharge at a concentration of 5 mg/d per model cell of aquifer, the ratio of potentially available carbon to the flux of DOC to the aquifer is:

$$\text{LTSR (yr/m}^3\text{)} = \frac{\text{AOC (mg/m}^3\text{)}}{\text{Flux of DOC (mg/yr)}}, \quad (5)$$

where LTSR (in units of years per meter cubed of sediment) may be termed the “long-term sustainability ratio” for the MNA of the system. Ideally, the LTSR would quantify the length of time organic carbon in a given volume of aquifer can sustain the DOC flux needed to maintain MNA. In practice, however, the physics and chemistry of DOC mobilization are far too complex to make this estimate quantitative. On the other hand, it is clear that when the LTSR is large, the long-term sustainability of MNA at a site will be proportionally large. Conversely, when the LTSR is small, the sustainability of MNA will be small.

In the case of the Kings Bay site, the LTSR is:

$$\text{LTSR} = \frac{5.9 \times 10^6 \text{ mg/m}^3}{365 \text{ mg/yr}} = 1.6 \times 10^4 \times \text{yr/m}^3. \quad (6)$$

This relatively large LTSR value illustrates that the amount of AOC in the system is large relative to the flux of DOC needed to sustain MNA. This, in turn, provides an explanation for the observed sustainability of MNA at the Kings Bay site for at least 20 years, and indicates that MNA could be sustained virtually indefinitely in this system.

Short-Term and Long-Term Sustainability

This analysis, which is based on simulations using a deterministic mass-balance model, indicates that the “sustainability” of MNA for chlorinated ethenes includes distinct short- and long-term components. The interaction of these components is illustrated in figure 19. When the short-term sustainability ratio (DO/DOC) is large, and the long-term sustainability ratio (AOC/DOC flux) is small, oxic conditions develop and MNA for chlorinated ethenes will be inherently unsustainable. When the STSR decreases below 1, anoxic conditions will develop and MNA will be sustainable for at least the short term. If the LTSR is too small, however, the amount of organic carbon may be insufficient to sustain MNA over the long term. When the STSR is small and the LTSR is large, MNA for chlorinated ethenes will be sustained over the long term. The threshold value of the LTSR needed to insure long-term (greater than 300 years) sustainability is not presently known. On the basis of this study, however, a value on the order of 10^4 yr/m^3 may be sufficient to meet the requirements of long-term sustainability.

Electron Acceptor Depletion and Sustainability

The simulations of PCE transport shown on figure 18 indicate that a high DO/DOC ratio (relatively reducing conditions) serves to limit the extent of the PCE plume as would be intuitively expected. Sometimes, however, model simulations can reveal behavior that is less intuitively obvious. For example, model simulations indicate that over relatively long timeframes (about 80 years), VC concentrations do not follow the pattern observed for PCE (fig. 18). Figure 20 shows simulated VC concentrations for different DO/DOC ratios. In this case, however, both highly reducing (DO/DOC ratio of 1/5) and oxic (DO/DOC ratio of 5/1) conditions were smaller than the intermediate (5/5 DO/DOC ratio) condition. For the highly reducing case, reductive dechlorination was capable of restricting VC transport, and thus the smaller VC plume. Similarly, under oxic conditions, oxic mineralization of VC restricted VC transport. For the intermediate condition, however, the amount of Fe(III) supporting anoxic mineralization of VC became limiting, which caused the VC plume to expand.

The simulations shown in figure 20 are probably not a realistic representation of the system as it now exists. Because of the Fenton's Reagent injection, a large amount of Fe(III) has been added to the system. Much of the previous sulfate-reducing portion of the plume (near the source area) is in fact now dominated by Fe(III) reduction as a result of the added ferric iron. Model simulations that increased the amount of Fe(III) present in the system prevented the increased size of the VC plume for the 5/5 ratio of DO/DOC shown in figure 20. Nevertheless, these simulations illustrate that the sustainability of MNA for chlorinated ethenes in general, and for VC in particular, may be subject to electron-acceptor limitations in addition to electron-donor limitations. As a result, these electron-acceptor limitations also should be considered in evaluations of sustainability.

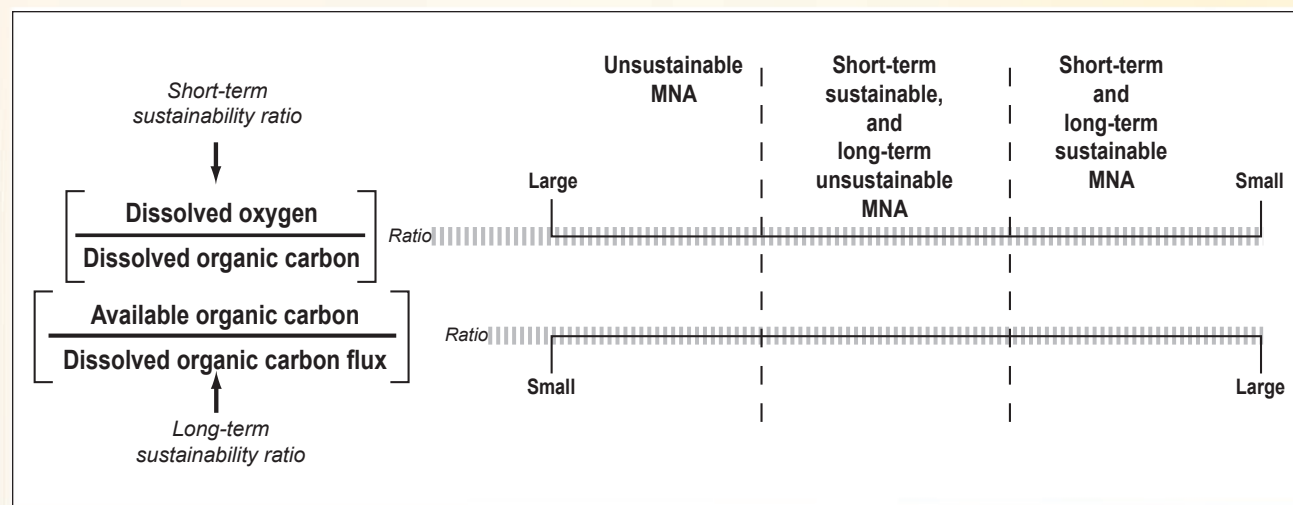
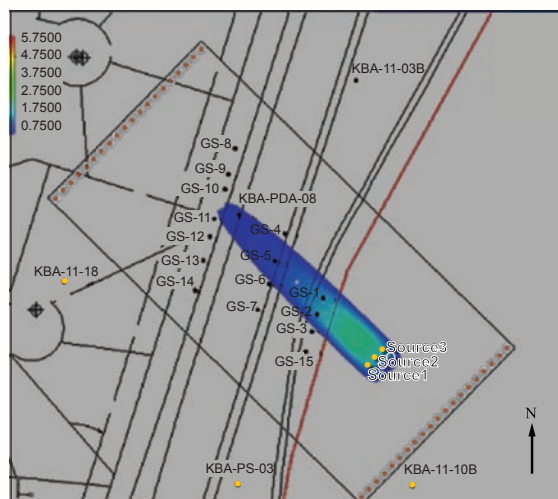
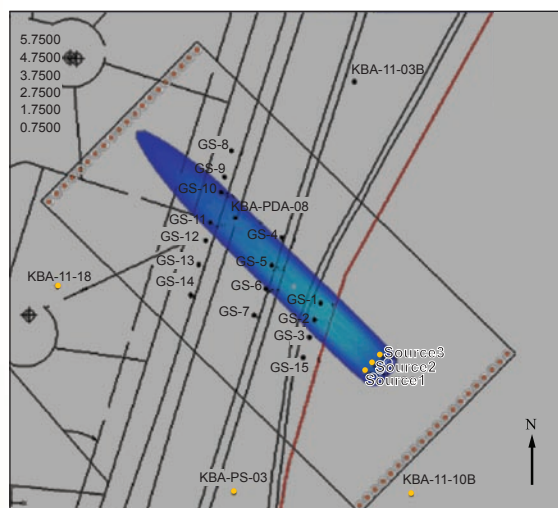
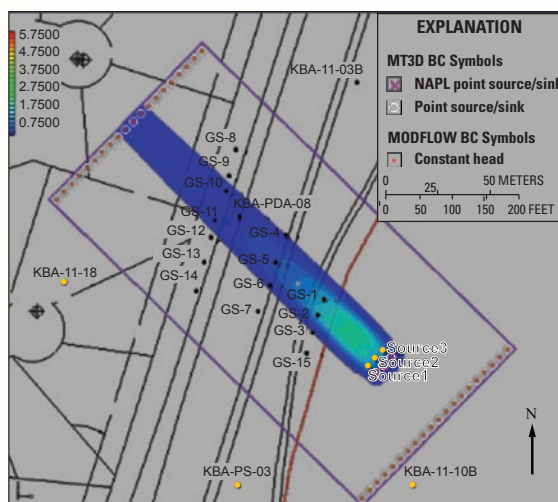


Figure 19. Diagram showing the short- and long-term components of the sustainability of monitored natural attenuation (MNA).

Table 3. Organic carbon content of Kings Bay sediments.

[mg/kg, milligrams per kilogram; —, not determined]

Sample horizon	Replicate analysis number	Weight loss on ignition ¹ (mg/kg)	Carbon content ² (mg/kg)	Extractable bioavailable organic carbon ³ (mg/kg)
Soil-zone sample, cored at well KBA-11-13A	1	460	940	80 ± 2
	2	450	—	260 ± 5
	3	700	—	20 ± 2
	4	—	—	80 ± 33
	5	—	—	60 ± 4
	Mean	540 ± 140	940	500 ± 20
Organic-matter-rich confining bed, outcrop samples	1	20,300	16,000	1,500 ± 68
	2	23,100	—	1,100 ± 73
	3	22,700	—	600 ± 74
	4	—	—	9,900 ± 830
	5	—	—	1,200 ± 61
	Mean	22,000 ± 1,500	16,000	14,300 ± 490
Organic-matter-rich confining bed, cored samples at well USGS-9	1	5,800	3,600	400 ± 170
	2	4,500	—	400 ± 11
	3	4,600	—	130 ± 1
	4	—	—	1,100 ± 115
	5	—	—	300 ± 19
	Mean	5,000 ± 700	3,600	2,300 ± 120

¹ Loss in weight of pre-dried samples after 8 hours at 400°C.² Elemental carbon analysis by catalytic combustion at 900°C.³ Extractable bioavailable organic carbon, mean is sum of five extractions shown.**1/5 DO/DOC ratio****5/1 DO/DOC ratio****5/5 DO/DOC ratio**Base modified from U.S. Geological Survey
1:24,000-scale digital data**Figure 20.** Simulated 2050 VC concentrations for DO/DOC ratios of 1/5, 5/5, and 5/1. All ratios are in milligrams per liter.

Conclusions

The sustainability of monitored natural attenuation (MNA) for any site and for any contaminant depends upon (1) the presence of chemical/biochemical processes capable of cycling contaminant(s) to innocuous byproducts, and (2) the availability of sufficient energy to drive these transformations to completion (fig. 6). By this definition, the example of the Kings Bay site meets all of the criteria for both short- and long-term sustainability of MNA for chlorinated ethenes. First, biochemical processes are in place (reductive dechlorination, VC oxidation) that transform chlorinated ethenes to innocuous byproducts. Secondly, sufficient energy exists in the form of organic carbon capable of driving these transformations to completion over the timeframe required (about 14 years).

The sustainability of natural attenuation for chlorinated ethenes can be quantitatively assessed by considering the mass and energy balance of ground-water systems. Such mass and energy balances can be made by using either empirical or deterministic methods. But regardless of the methods used, it is necessary to:

1. Quantify the flux of ground water moving through the system. Any assessment of mass and energy balance is highly sensitive to ambient rates of ground-water flow, and it is important for this parameter to be highly constrained.
2. Delineate the mass and distribution of chlorinated ethenes and/or NAPL present in the system. A true mass balance cannot be achieved without estimates of contaminant mass. While such estimates are difficult to make and are subject to considerable uncertainty, the sustainability of MNA cannot be assessed without them. A variety of methods are available for making these estimates. Given an estimated mass of NAPL present, it is possible to estimate the time of remediation (TOR) needed for a contamination to completely disperse.
3. Quantify the mass and flux of available electron acceptors, especially dissolved oxygen, being delivered to the system. Oxygen can divert electron flow from chlorinated ethene reduction; understanding the dynamics of electron-acceptor delivery to the system is fundamental to quantifying MNA sustainability.
4. Quantify the mass and flux of available organic carbon. Microbially utilizable organic carbon in soil and aquifer sediments can be estimated using sediment-extraction procedures. Similarly, measurements of dissolved organic carbon provide an estimate of carbon mass present in the aqueous phase.
5. Assess the interaction of electron donors and acceptors. The short-term sustainability of MNA for chlorinated ethenes requires that the molar ratio of dissolved oxygen to dissolved organic carbon to a system be less than 1. The long-term sustainability of MNA requires that the

ratio of available organic carbon in a system be large relative to the flux of organic carbon needed to maintain anoxic conditions.

The importance of sustainability when assessing MNA has only recently been identified as an important issue in environmental remediation (Newell and Aziz, 2004). The framework outlined in this report provides methods for assessing and quantifying the sustainability of MNA for chlorinated ethenes.

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Appendix 1. Description of the Deterministic Model

The SEAM3D code uses mathematical representations of contaminant loading and attenuation processes, and sums them in order to provide a quantitative mass and energy balance. Advection refers to dissolved mass carried by flowing ground water, and is proportional to the velocity of ground-water flow v [LT^{-1}] and the change of concentration mass [ML^{-3}] over a particular distance, x [L^{-1}]:

$$-v \frac{\partial C}{\partial x}.$$

This advective term, therefore, has units of mass concentration per unit time [$\text{ML}^{-3}\text{T}^{-1}$]. The dispersion of dissolved mass in flowing ground water is proportional to a scale-dependent constant, the coefficient of dispersion (D) [L^2T^{-1}], and the second derivative of the concentration gradient:

$$D \frac{\partial^2 C}{\partial x^2}.$$

Again, the units of this term are mass concentration per unit time [$\text{ML}^{-3}\text{T}^{-1}$]. Sorption refers to the distribution of a mass between the aqueous and adsorbed phases and can be described by the term:

$$-\frac{\rho_b K_d}{n} \frac{\partial C}{\partial t},$$

where ρ_b is the average bulk density of aquifer solids [ML^{-3}]; n is aquifer porosity (dimensionless); and K_d is a distribution coefficient describing solute partition between the adsorbed and dissolved state [L^3M^{-1}]. The units of this term are also in mass concentration per unit time [$\text{ML}^{-3}\text{T}^{-1}$].

The microbial transformation of electron donors and acceptors is evaluated by summing the effects of microbial colonies inhabiting the ground-water system on substrates and electron acceptors (EA). For each substrate degraded by microbial population x , the sink term is

$$R_{\text{sink},ls}^{\text{bio}} = \sum_x \frac{M_x}{\theta} r_{x,ls}, \quad (1.1)$$

where θ is the effective porosity (dimensionless); M_x is the microbial biomass concentration [$\text{M}_b \text{L}_{\text{pm}}^{-3}$] for $x = 1, 2, \dots, \text{NM}$ (number of microcolonies); and $r_{x,ls}$ is the utilization rate of substrate ls in microbial population x where the units of this term are in mass concentration per unit time [$\text{M}_{ls} \text{M}_b^{-1} \text{T}^{-1}$]. For each electron acceptor, the sink term is

$$R_{\text{sink},le}^{\text{bio}} = \sum_x \frac{M_x}{\theta} r_{x,le}. \quad (1.2)$$

The utilization of each substrate within microbial population x is described by the equation

$$r_{x,ls} = \sum_{le} \nu_{x,ls,le}, \quad (1.3)$$

where $\nu_{x,ls,le}$ is the specific rate of substrate utilization for microbial population x growing on substrate ls and electron acceptor le . Similarly, utilization of each electron acceptor follows

$$r_{x,le} = \sum_{ls} \gamma_{x,ls,le} \nu_{x,ls,le}, \quad (1.4)$$

where $\gamma_{x,ls,le}$ is the electron-acceptor use coefficient [$\text{M}_{le} \text{M}_{ls}^{-1}$]. Finally, Monod kinetics are used to describe substrate and electron-acceptor utilization

$$\nu_{x,ls,le} = \nu_{x,ls,le}^{\text{max}} \left[\frac{\bar{S}_{ls}}{\bar{K}_{x,ls,le}^s + \bar{S}_{ls}} \right] \left[\frac{\bar{E}_{le}}{K_{x,le}^e + \bar{E}_{le}} \right] N_x I_{le,li}, \quad (1.5)$$

where $\nu_{x,ls,le}^{\text{max}}$ is the maximum specific rate of substrate utilization for microbial population x growing on substrate ls and electron acceptor le [$\text{M}_{ls} \text{M}_b^{-1} \text{T}^{-1}$]; $\bar{K}_{x,ls,le}^s$ is the half-saturation constant for substrate ls for utilization of electron acceptor le [$\text{M}_{ls} \text{L}^{-3}$]; $K_{x,le}^e$ is the effective half-saturation constant for electron acceptor le [$\text{M}_{le} \text{L}^{-3}$]; and \bar{S}_{ls} and \bar{E}_{le} are the effective concentrations of substrate ls [$\text{M}_{ls} \text{L}^{-3}$] and electron acceptor le [$\text{M}_{le} \text{L}^{-3}$], respectively, (defined as the difference between the aqueous phase concentrations and minimum concentrations below which biodegradation ceases).

The model code, SEAM3D, uses inhibition functions to simulate the preferential utilization of electron acceptors in the order $\text{O}_2 > \text{NO}_3 > \text{Mn(IV)} > \text{Fe(III)} > \text{SO}_4 > \text{CO}_2$, an order that corresponds to the decreasing free energy available to microorganisms from each reaction. When concentrations of oxygen are above a given threshold (about 0.5 mg/L), the model inhibits the oxidation of competing electron acceptors using a function $I_{le,li}$ defined by

$$I_{le,li} = 1 \text{ for } le=1, \quad (1.6)$$

and

$$I_{le,li} = \prod_{li=1}^{le-1} \left[\frac{\kappa_{le,li}}{\kappa_{le,li} + \bar{E}_{li}} \right] \text{ for } le = 2, 3, 4, 5, \text{ or } 6, \quad (1.7)$$

where $\kappa_{le,li}$ is the electron-inhibition coefficient [$M_e L^{-3}$], representing inhibition of electron acceptor le by electron acceptor li . Thus, the model is able to simulate the order of electron-acceptor utilization observed in natural systems (fig. 8).

Finally, the rate of dissolution of the NAPL mass $R_{Source,ls}^{NAPL}$ can be formulated in terms of the maximum concentration of a solute in equilibrium with a NAPL of given composition (C_{ls}^{eq}) as given by Raoult's law:

$$C_{ls}^{eq} = f_{ls} (C_{ls}^{sol}), \quad (1.8)$$

where f_{ls} is the mole fraction of the solute and C_{ls}^{sol} is the solubility of the solute, and the actual concentration at any given point in space (C_{ls}) is:

$$R_{Source,ls}^{NAPL} = k^{NAPL} (C_{ls}^{eq} - C_{ls}), \quad (1.9)$$

where k^{NAPL} is the NAPL dissolution rate constant (T^{-1}). This gives $R_{Source,ls}^{NAPL}$ in units of contaminant concentration per unit time [$ML^{-3}T^{-1}$].

The individual processes that affect any particular solute in ground-water systems, including hydrodynamic dispersion, advection, sorption, and biodegradation, and NAPL dissolution then can be summed giving an explicit mass balance governing the transport of any particular solute. In the case of chlorinated ethenes, the general mass-balance equation may be written:

$$-v_i \frac{\partial S_{ls}}{\partial x_i} + \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial S_{ls}}{\partial x_j} \right) + \frac{q_s}{\theta} S_{ls}^* - R_{sink,ls}^{bio} + R_{source,ls}^{NAPL} = R_{ls} \frac{\partial S_{ls}}{\partial t}, \quad (1.10)$$

where

- S_{ls} is the aqueous phase chlorinated ethene concentration [$M_{ls} L^{-3}$] for $ls=1,2,\dots,NS$ (number of individual chlorinated ethenes);
- S_{ls}^* is the chlorinated ethene point-source concentration [$M_{ls} L^{-3}$];
- v_i is the average pore-water velocity [LT^{-1}];
- x_i is distance [L];
- D_{ij} is the tensor for the hydrodynamic dispersion coefficient [$L^2 T^{-1}$];
- $R_{sink,ls}^{bio}$ is a biodegradation sink term dependent on the mode of respiration [$M_{ls} L^{-3} T^{-1}$];
- $R_{source,ls}^{NAPL}$ is a term associated with non-aqueous phase liquid (NAPL) dissolution [$M_{ls} L^{-3} T^{-1}$];
- R_{ls} is the retardation factor for chlorinated ethene ls [L^0];
- t is time [T];
- θ is aquifer porosity [L^0]; and
- q_s is the volumetric flux of water per unit volume of aquifer [T^{-1}] with $q_s > 0$ for sources and $q_s < 0$ for sinks.

In the same manner, mass-balance equations can be written for dissolved organic carbon serving as electron donors in the system, and for the various soluble and insoluble compounds serving as electron acceptors. This set of coupled equations then can be solved simultaneously to assess electron donor oxidation coupled to electron acceptor reduction, and thus the flow of energy through the system.

Appendix 2. Parameters Used to Simulate the Kings Bay Site

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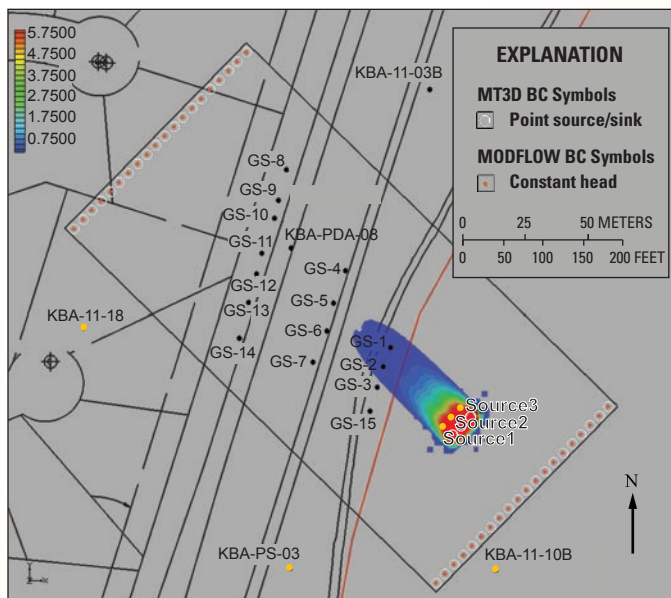
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Boundary Conditions and Hydrologic Parameters

The site was modeled with one layer representing a semi-confined aquifer to which a non-aqueous phase liquid (NAPL) source had been delivered (fig. 10). The conceptualization shown in figure 10 was translated into a deterministic model by applying the Basic Transport, Advection, Dispersion, NAPL Dissolution, Source-Sink, Chemical Reaction, Biodegradation, and Reductive Dechlorination Packages of the SEAM3D model code. The steady-state flow field is constructed to represent the long-term average flow conditions at the site of the contamination in order to test the concept of monitored natural attenuation with SEAM3D over multi-decade time scales. Thus, the finite-difference grid is site specific with 20 columns and 40 rows with cell dimensions of 5 m by 5 m (an area of 20,000 m², shown on figure 2.1). The upgradient and downgradient boundaries were simulated as constant-head boundaries to match the observed head gradient across the plume in the semiconfined aquifer. The upgradient boundary is near a ground-water divide identified previously at the site (Leeth, 1999) and is treated as a constant head based on the average head at this boundary. The downgradient boundary was placed in the housing subdivision where water-level fluctuations are buffered by the presence of several small ponds. The lateral boundaries were placed perpendicular to observed lines of equal hydraulic head at the site, which is consistent with their treatment as no-flow boundaries. The water-table aquifer above the semiconfined aquifer was not actively simulated; however, the effect of recharge to the underlying semiconfined aquifer was simulated using the Source-Sink Package of SEAM3D.



Base modified from U.S. Geological Survey
1:24,000-scale digital data

Figure 2.1. Location of SEAM3D model area and boundary conditions.

SEAM3D uses the steady-state flow field created by MODFLOW, given concentration initial conditions and boundary conditions for the reactive transport model. A constant value of hydraulic conductivity (10 m/d) was assigned for the MODFLOW model based on estimates derived from aquifer tests conducted at the site (Leeth, 1999). The site-specific flow model is simplified; the average flow through the site is constrained by using the average known gradient across the site (commonly referred to as Darcy velocity); however, the pore velocity is determined by dividing the Darcy velocity determined by MODFLOW by the porosity. A constant porosity of 0.3 was applied in the model. The site-specific effective porosity is unknown (Leeth, 1999), so the value of 0.3 was selected as representative of the type of sediments encountered at the site (Fetter, 1988). A specific storage (0.0001 1/meter) and specific yield (0.1 dimensionless) were assigned (table 2.1) based on estimates made from aquifer tests at the site (Leeth, 1999).

In the Source-Sink Package of SEAM3D, recharge to the semiconfined aquifer was simulated using areally constant values, and recharge was considered to contain constant concentrations of the electron acceptors dissolved oxygen (5 mg/L) and sulfate (10 mg/L). In addition, areal recharge was considered to contain dissolved organic carbon mobilized from the soil zone and from the organic-matter-rich layer overlying the semiconfined aquifer (table 2.2). Because the amount of areal recharge delivered to the semiconfining aquifer was not directly measured, rates of electron acceptor-bearing recharge to the aquifer were adjusted as the model was constrained.

Solute Transport Parameters: The Dispersion Package

Given the ground-water velocity flow field generated by the MODFLOW-computed hydraulic gradient and an assigned porosity, the dispersion coefficient is calculated from the assigned dispersivity (5.0 m) and the ratio of transverse to longitudinal dispersivity (0.01). The effective molecular diffusion coefficient, which for sites dominated by advective ground-water flow is typically much less than the dispersion, was set to 5.0×10^{-5} m²/d (table 2.1).

Table 2.1. Hydrologic and dispersion parameters used in the SEAM3D model.

[m/d, meter per day; m, meter; m²/d, square meter per day]

Model parameter	Model input
Hydraulic conductivity	10 m/d
Porosity	0.3
Specific storage	0.0001 1/meter
Specific yield	0.1 (dimensionless)
Longitudinal dispersivity	5.0 m
Transverse dispersivity	0.05 m
Molecular diffusion coefficient	5.0×10^{-5} m ² /d

Table 2.2. Initial conditions, concentrations at the landfill boundary, and recharge concentrations for electron donors, electron acceptors, tracer, and biodegradation end products.

[mg/L, milligram per liter; O₂, dissolved oxygen; Fe(III), ferric iron; SO₄, sulfate; Fe(II), ferrous iron; CH₄, methane; Cl, chloride; N/A, not applicable]

Constituent	Concentrations (mg/L)		
	Initial	Boundary	Recharge
Electron donor	0.1	0.1	5.0
O ₂	0.0	0.0	5.0
⁽¹⁾ Fe(III)	50.0	N/A	N/A
SO ₄	1.0	1.0	10.0
Tracer	0.0	5.0	0.0
Fe(II)	0.0	1.0	0.0
CH ₄	0.0	2.0	0.0
Cl	0.0	0.0	0.0

⁽¹⁾ Unit for Fe(III) is milligrams per gram.

Sources of Dissolved Chlorinated Ethenes: The NAPL Dissolution Package

An important capability of the SEAM3D code is that it includes a NAPL Package designed to simulate the dissolution and mobilization of chlorinated ethenes from the NAPL present in the contaminant source area. This feature, when combined with the Biodegradation and Reductive Dechlorination Packages, allows simulation of a global mass balance that includes mineral and dissolved electron acceptors, dissolved organic carbon substrate, and the dissolution and natural attenuation of chlorinated ethenes. This capability, in turn, makes it possible to estimate times of remediation associated with NAPL dissolution, and thus, to assess the sustainability of natural attenuation.

The SEAM3D model allows NAPL dissolution to be conceptualized by assigning a given NAPL mass (C^N in grams per gram) to model cells according to the equation

$$C^N = M_{cell}^N / \rho_b V_{cell}, \quad (2.1)$$

where M_{cell}^N mass of NAPL is assigned to each model cell (g); V_{cell} is the volume of the cell ($\Delta x \times \Delta y \times$ NAPL thickness); and ρ_b (g/m³) is the sediment bulk density. SEAM3D then partitions the soluble components of the NAPL into the aqueous phase at each time step depending on the contaminant mass fraction of the NAPL, the molecular weight, solubility, rates of ground-water flow, and a NAPL dissolution constant. Depending on the amount of dissolution, the model then recalculates the amount of remaining NAPL for the next time step.

NAPL at the site was considered to contain both PCE (molecular weight of 166; solubility of 150 mg/L; initial mass fraction of 0.15) and TCE (molecular weight of 131; solubility of 1,100 mg/L; initial mass fraction of 0.01). These two contaminants were considered to coexist with an inert fraction of NAPL with a molecular weight of 150, and an initial NAPL

dissolution rate constant of 0.01 d⁻¹. This rate constant was chosen primarily because it is sufficiently fast so that hydrologic (rate of ground-water flow) and chemical (solubility) conditions would determine the overall rate of NAPL dissolution.

Estimating the mass of NAPL originally emplaced in an aquifer is necessary to make a true mass balance of the system. At the Kings Bay site, eyewitness accounts of waste-disposal practices are available, although written records of how much waste was disposed are not available. One eyewitness account recalled that the waste-disposal trenches were dug with a backhoe to a depth of between 6 and 8 feet, trucks delivering municipal waste filled the trenches, and the backhoe then covered the trenches with sand. Apparently, drums of PCE waste were disposed of in this fashion. Given the waste-disposal practices employed, the measured size of the PCE source areas (Chapelle and Bradley, 1998) and the approximate concentrations of PCE measured in the source area place some constraints on the mass of NAPL emplaced. Nevertheless, because of the inherent uncertainties associated with estimating NAPL mass, a range of values was simulated.

Based on an approximate 5- by 15-m area of the source zone (75 m²), a thickness of affected aquifer of 1 m, measured concentrations of PCE ranging between 1 and 10 milligrams per gram (mg/g) of sediment, and a sediment bulk density of 1.85×10^6 g/m³ suggest that between 280 and 2,800 kg of PCE were disposed of at the site. Because one 55-gallon barrel of PCE weighs about 280 kg, one could assume that between 1 and 10 barrels of waste PCE were disposed of at this site. Assuming that one barrel of PCE is assigned to each source-area model cell ($M_{cell}^N = 280,000$ g), that a cell area is 25 m², a NAPL thickness is 1 m, and the ρ_b is 1.85×10^6 g/m³, the C^N calculated from equation 2.1 would be 0.006 g/g. These estimates were used as the starting point for assigning an amount of PCE NAPL in the modeled source area, and then were refined as the model was constrained with available hydrologic and geochemical data.

Geochemical and Redox Parameters: The Biodegradation Package

Redox conditions at the Kings Bay site have previously been shown to be dominated by Fe(III) reduction and sulfate reduction. Four redox processes (oxygen reduction, Fe(III) reduction, sulfate reduction, and methanogenesis) were incorporated into the SEAM3D simulation of the site. All of these electron-accepting processes were coupled to the oxidation of a soluble electron donor (dissolved organic carbon of oxidation state zero and a molecular weight of 32). To activate these processes in the model, the species oxygen, sulfate, Fe(II), and methane were defined so that SEAM3D would write a mass-balance equation for each species. SEAM3D is designed to consider Fe(III) reduction occurring with solid-phase Fe(III) oxyhydroxides. Near the landfill, where sulfate-reducing conditions were observed, the Fe(III) content of aquifer material was set to zero. Downgradient, where Fe(III)-reducing conditions were observed, the Fe(III) content of

aquifer materials was set to an initial value of 50 micrograms per kilogram ($\mu\text{g/kg}$). This value was based on measurements of Fe(III) made in a shallow coastal-plain aquifer with similar hydrology to that of Kings Bay (Chapelle and others, 2002). SEAM3D computes a mass balance on Fe(III) for each time step as Fe(III) reduction occurs over time, allowing the amount of Fe(III) present in the system to decrease as Fe(III) reduction proceeds. This feature makes it possible to assess how the consumption of Fe(III) in the system affects the sustainability of natural attenuation.

A large number of parameters are required by SEAM3D in order to simulate the biodegradation of dissolved organic carbon coupled to the sequential reduction of oxygen, Fe(III), sulfate, and carbon dioxide. These include specifying the density of aerobic, Fe(III)-reducing, sulfate-reducing, and methanogenic microorganisms (grams per cubic centimeter); specifying the inhibition coefficients directing sequential utilization; specifying product generation coefficients for Fe(II) and methane; specifying Monod half-saturation constants for each electron-accepting process coupled to dissolved organic carbon (substrate) utilization; and specifying Monod maximum utilization rate constants for each electron-accepting process. The problem was simplified by assuming that the microbial population is at steady state (rate of death equals rate of growth). The parameter values used to build the biodegradation package in the model are shown in table 2.3.

Chlorinated Ethene Transformation Parameters: The Reductive Dechlorination Package

The transformation of chlorinated ethenes was simulated within SEAM3D by assigning Monod kinetic parameters (equation 1.5), which describe reductive dechlorination for each species. In addition, the anaerobic oxidation of VC was simulated. At the Kings Bay site, ethene, the final degradation product of reductive dechlorination, is generally below detectable levels (0.01 mg/L), although occasional detections (about 0.1 mg/L) have been noted. If reductive dechlorination

to ethene were the only biodegradation process occurring, then ethene concentrations should be on the order of 1,000 $\mu\text{g/L}$ for much of the plume. There are two possible explanations for this discrepancy. First, VC may be reduced to ethene, which is then rapidly mineralized to carbon dioxide, preventing the accumulation of ethene in solution. Secondly, VC may be directly mineralized to carbon dioxide (Bradley, 2000). The occasional detections of ethene show that a component of VC reduction to ethene occurs at the site; however, the observation that DCE (the source of VC) is transported farther downgradient than VC indicates that VC is subject to anoxic mineralization as well. The SEAM3D code is capable of simulating both reductive and oxidative transformation of all chlorinated ethenes. At the Kings Bay site, reductive dechlorination was simulated for all four chlorinated ethenes, and anoxic mineralization was simulated only for VC.

The Monod kinetic parameters used to simulate chlorinated ethene transformation at the Kings Bay site are shown in table 2.4. Half-saturation constants (K) and maximum rates of substrate uptake (ν) for each reductive process were assigned. Only VC was considered subject to anoxic mineralization. Thus, half-saturation constants for direct mineralization of PCE, TCE, and DCE were set to zero, and a finite value was assigned for VC mineralization coupled to Fe(III) reduction.

The sequential reduction of PCE, TCE, DCE, and VC was simulated by assigning inhibition factors for each process. Since oxygen reduction strongly inhibits the reduction of all chlorinated ethenes, the inhibition factors for oxygen were set relatively low (table 2.5). Conversely, because electron-accepting processes such as Fe(III) reduction, sulfate reduction, and methanogenesis are not observed to inhibit reductive dechlorination (Bradley, 2000), the inhibition concentrations are assigned larger values. Finally, the stoichiometric conversion factors for the various products of chlorinated ethene reduction, which allow model output in units of milligrams per liter, are shown in table 2.6.

Table 2.3. Initial concentration of microbial populations and biodegradation parameters for four terminal electron-accepting processes.

[O_2 , oxygen; Fe(III), ferric iron; SO_4 , sulfate; g m^{-3} , grams per cubic meter; d^{-1} , 1/day; g g^{-1} , gram per gram]

Microbial population	M_x	$\nu_{x,s,le}^{max}$	$\bar{K}_{x,s,le}^s$	$\bar{K}_{x,le}^e$	$Y_{x,ls,le}$	$\gamma_{x,ls,le}$	ζ_x	$K_{le,li}^{(1)}$		
	(g m^{-3})	(d^{-1})	(g m^{-3})	(g m^{-3})	(g g^{-1})	(g g^{-1})	(g g^{-1})	O_2	Fe(III)	SO_4
Aerobes	0.25	0.05	5.0	1.0	0.0	3.0	N/A	N/A	N/A	N/A
Iron reducers	0.025	0.05	10.0	N/A	0.0	33.0	0.10	10.0	N/A	N/A
Sulfate reducers	0.025	0.005	10.0	1.0	0.0	4.5	N/A	10.0	50.0	N/A
Methanogens	0.025	0.01	10.0	N/A	0.0	N/A	0.20	10.0	25.0	1.0

⁽¹⁾ Units for inhibition coefficients are in milligrams per liter, except for Fe(III), which is in milligrams per gram.

Table 2.4. Initial concentration of PCE/TCE and DCE/VC degraders and kinetic reductive dechlorination parameters for the simulated chlorinated ethenes.

[O₂, oxygen; Fe(III), ferric iron; SO₄, sulfate; PCE, perchloroethene; TCE, trichloroethene; DCE, dichloroethene; VC, vinyl chloride; g m⁻³, grams per cubic meter; d⁻¹, 1/day; N/A, not applicable]

Chlorinated ethene	M_y (g m ⁻³)	$\nu_{lc}^{\max,EA}$ (d ⁻¹)	\bar{K}_{lc}^e (g m ⁻³)	$\kappa_{le,li}^{(1)}$					
				O ₂	Fe(III)	SO ₄	PCE	TCE	DCE
PCE	0.025	0.60	5.0	0.5	100	50	N/A	N/A	N/A
TCE		1.0	10.0	0.5	100	50	50	N/A	N/A
DCE	0.025	1.2	20.0	1.0	25	50	50	10	N/A
VC		0.5	15.0	1.0	25	50	50	10	1.0

⁽¹⁾ Units for inhibition coefficients are in milligrams per liter except for Fe(III), which is in milligrams per gram.

Table 2.5. Biodegradation parameters for net mineralization of DCE and VC.

[DCE, dichloroethene; VC, vinyl chloride; d⁻¹, 1/day; g m⁻³, grams per cubic meter; g g⁻¹, gram per gram; N/A, not applicable]

Microbial population	DCE					VC				
	$\nu_{x,lc,le}^{\max}$ (d ⁻¹)	$\bar{K}_{x,lc,le}^{ed}$ (g m ⁻³)	$\bar{K}_{x,le}^e$ (g m ⁻³)	$Y_{x,lc,le}$ (g g ⁻¹)	$\gamma_{x,lc,le}$ (g g ⁻¹)	$\nu_{x,lc,le}^{\max}$ (d ⁻¹)	$\bar{K}_{x,lc,le}^{ed}$ (g m ⁻³)	$\bar{K}_{x,le}^e$ (g m ⁻³)	$Y_{x,lc,le}$ (g g ⁻¹)	$\gamma_{x,lc,le}$ (g g ⁻¹)
Aerobes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Iron reducers	0.0	0.0	0.0	0.0	0.0	0.08	1.0	N/A	0.0	0.0

Sorption Parameters: The Chemical Reaction Package

In addition to hydrologic and microbiologic transformations, the mass balance of solutes in the semiconfined aquifer is subject to geochemical processes as well. All solutes are subject to chemical and electrical interactions with aquifer materials. These interactions, which are highly complex and not well-understood, are typically lumped together and modeled as sorption processes. The SEAM3D code allows consideration of sorption processes on the transport of solutes in the Chemical Reaction Package.

SEAM3D enables the user to use different approaches to modeling sorption including specifying linear and Freundlich adsorption isotherms. For the Kings Bay model, a linear

isotherm coefficient was specified for each mobile chlorinated ethene, substrate, and product considered in the mass balance. In addition, a tracer was specified and assigned a sorption coefficient to help constrain rates of ground-water flow. The retardation factors for chlorinated ethenes were estimated from the approximate organic matter content of aquifer material and appropriate octanol/water partition coefficients. The solutes and adsorption isotherm coefficients are shown in table 2.7. Most of the biochemically active solutes such as dissolved oxygen and substrate were considered to be nonsorbing. Sulfate, however, is known to be slightly retarded relative to ground-water flow. Because sulfate transport was used to constrain rates of ground-water flow in the model, a sorption coefficient was specified. In addition, a tracer was specified with the same sorption coefficient as sulfate.

Table 2.6. Stoichiometric conversion factors for reductive dechlorination.

[PCE, perchloroethene; TCE, trichloroethene; Cl, chloride; DCE, dichloroethene; VC, vinyl chloride]

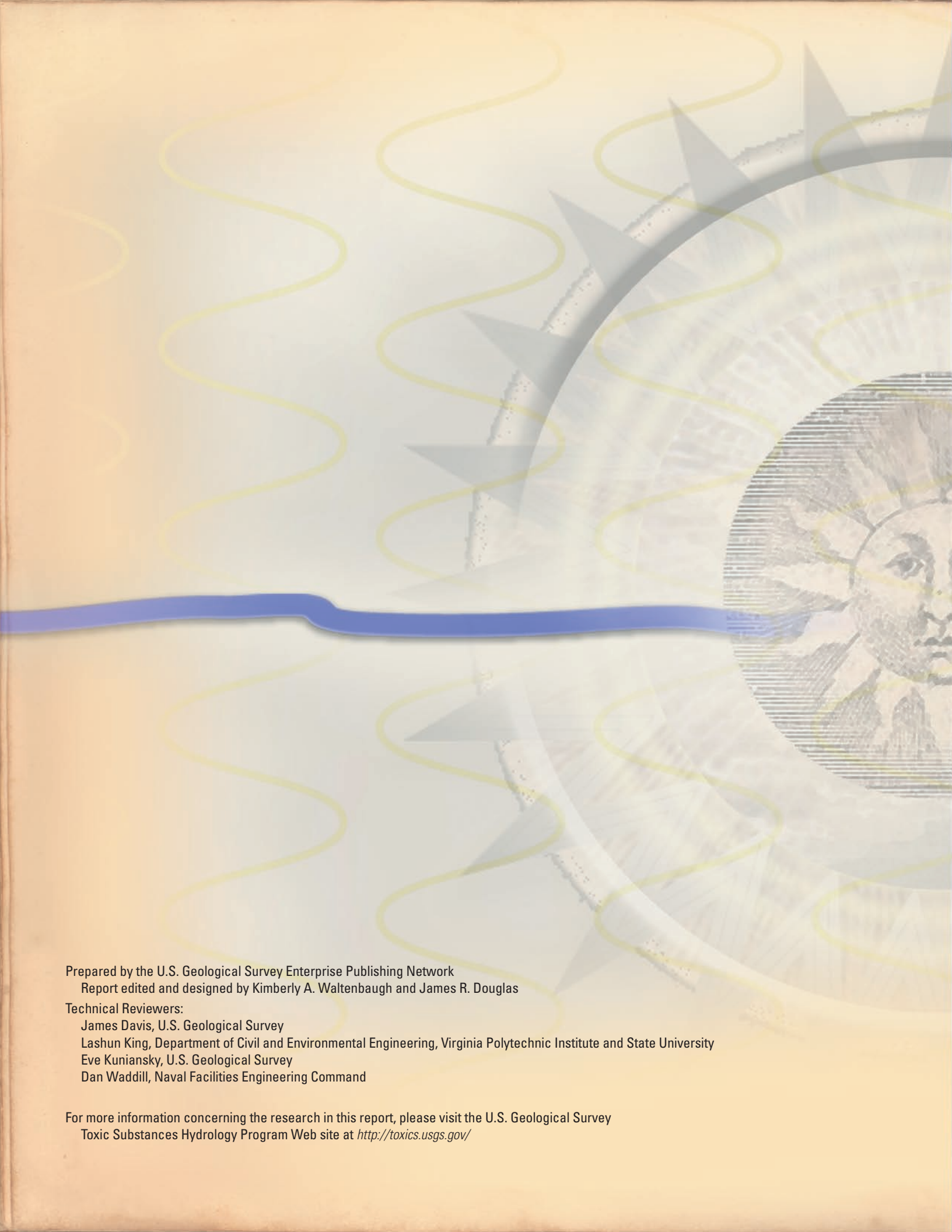
Reaction	Stoichiometric factor
PCE→TCE	0.7923
PCE→Cl	0.2141
TCE→DCE	0.7379
TCE→Cl	0.270
DCE→VC	0.6447
DCE→Cl	0.3662
VC→Cl	0.568
VC→Ethene	0.4498

Table 2.7. Sorption parameters for mobile constituents.

[m³/d, cubic meters per day; O₂, oxygen; SO₄, sulfate; Fe(II), ferrous iron; CH₄, methane; PCE, perchloroethene; TCE, trichloroethene; DCE, dichloroethene; VC, vinyl chloride; Cl, chloride]

Constituent	Distribution coefficient (m ³ /d)	Retardation factor ¹
Electron donor	0.0	1.0
O ₂	0.0	1.0
SO ₄	8.11 x 10 ⁻⁸	1.50
Tracer	8.11 x 10 ⁻⁸	1.50
Fe(II)	0.0	1.0
CH ₄	0.0	1.0
PCE	6.08 x 10 ⁻⁷	4.75
TCE	3.08 x 10 ⁻⁷	2.90
DCE	1.59 x 10 ⁻⁷	1.98
VC	1.95 x 10 ⁻⁷	2.20
Ethene	0.0	1.0
Cl	0.0	1.0

¹ Bulk density = 1.85 x 10⁶ grams per cubic meter; total porosity = 0.30.



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$$R_{sink,de}^{bio} = \sum_x \frac{M_x}{\theta} r_{x,de} \quad (1.2)$$

is the total rate of utilization of each substrate within microbial population x described by the equation

$$r_{x,ls} = \sum_{le} \nu_{x,ls,de} \quad (1.3)$$

is the specific rate of substrate utilization for population x growing on substrate ls and electron acceptor le . Similarly, utilization of each electron acceptor

$$r_{x,de} = \sum_{ls} \gamma_{x,ls,de} \nu_{x,ls,de} \quad (1.4)$$

is the electron acceptor use coefficient [$M_e M_s^{-1}$]. Monod kinetics are used to describe substrate and electron acceptor utilization

$$\nu_{x,ls,de} = \frac{\bar{S}_{ls}}{K_{x,ls,de} + \bar{S}_{ls}} \left[\frac{\bar{E}_{le}}{K_{x,de}^e + \bar{E}_{le}} \right] N_x I_{le,li} \quad (1.5)$$

is the maximum specific rate of substrate utilization of microbial population x growing on substrate ls and electron acceptor le [$M_s M_p^{-1} T^{-1}$]; $K_{x,ls,de}^s$ is the half-saturation constant of substrate ls for utilization of electron acceptor le [M_s]; $K_{x,de}^e$ is the effective half-saturation constant for electron acceptor le [$M_e L^{-3}$]; and \bar{S}_{ls} and \bar{E}_{le} are the effective concentrations of substrate ls [$M_s L^{-3}$] and electron acceptor le [$M_e L^{-3}$], respectively, (defined as the difference between phase concentrations and minimum concentrations at which biodegradation ceases).

The model code, SEAM3D, uses inhibition functions to describe preferential utilization of electron acceptors in the order $O_2 > Mn(IV) > Fe(III) > SO_4 > CO_2$, an order that corresponds to the decreasing free energy available to microorganisms in each reaction. When concentrations of oxygen are above a given threshold (about 0.5 mg/L), the model describes competition of competing electron acceptors using a function defined by

$$I_{le,li} = 1 \text{ for } le=1, \quad (1.6)$$

$$I_{le,li} = \prod_{li=1}^{le-1} \left[\frac{K_{le,li}}{K_{le,li} + \bar{E}_{li}} \right] \text{ for } le = 2,3,4,5 \text{ or } 6, \quad (1.7)$$

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